

# PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>M150/WO/005</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/IB 99/ 00207</b>	International filing date (day/month/year) <b>08/02/1999</b>	(Earliest) Priority Date (day/month/year) <b>09/02/1998</b>
Applicant <b>M3D SOCIETE ANONYME</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

**4. With regard to the title,**



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

**5. With regard to the abstract,**



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

**6. The figure of the drawings to be published with the abstract is Figure No.**



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.



None of the figures.



## INTERNATIONAL SEARCH REPORT

International Application No.

IB 99/00207

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G77/42 C08L83/10 C08L61/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ✓	US 4 657 951 A (TAKARADA MITSUHIRO ET AL) 14 April 1987 see claims 1-6 ---	1,2,4-6, 14
X ✓	US 3 911 045 A (HARTMANN PETER ET AL) 7 October 1975 see claim 1 see column 2, line 33 - line 60 ---	1
X ✓	WO 96 33238 A (AMERON INC ;KANE JOHN F (US); MOWRER NORMAN R (US)) 24 October 1996 see claims 1-43 see page 3, line 3 - line 4 see page 16, line 16 - line 31 see page 36, line 25 - line 30 --- -/--	1,2,4-6

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&amp;" document member of the same patent family

Date of the actual completion of the international search

21 April 1999

Date of mailing of the international search report

04/05/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Depijper, R



## INTERNATIONAL SEARCH REPORT

International Application No.

IB 99/00207

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A ✓	WO 97 19977 A (BP CHEM INT LTD) 5 June 1997 see claims 1-10 ---	1
X	DE 16 94 974 A (STENBECK G) 26 August 1971 see claim 1 see page 1, paragraph 3 see page 3; example 1 -----	1



## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 99/00207

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4657951	A	14-04-1987	JP 2015978 C	19-02-1996
			JP 6092524 B	16-11-1994
			JP 61192711 A	27-08-1986
US 3911045	A	07-10-1975	DE 2306463 A	29-08-1974
			AU 476576 B	30-09-1976
			AU 6525674 A	07-08-1975
			BE 810720 A	07-08-1974
			CA 1033491 A	20-06-1978
			CS 175473 B	31-05-1977
			DD 111395 A	12-02-1975
			FR 2217376 A	06-09-1974
			GB 1424290 A	11-02-1976
			JP 1047903 C	28-05-1981
			JP 49113000 A	28-10-1974
			JP 55039183 B	08-10-1980
			NL 7401649 A	13-08-1974
			ZA 7400835 A	24-12-1974
WO 9633238	A	24-10-1996	US 5736619 A	07-04-1998
			AU 699446 B	03-12-1998
			AU 5558396 A	07-11-1996
			BR 9608196 A	21-07-1998
			CA 2218694 A	24-10-1996
			CZ 9703331 A	17-06-1998
			EP 0821711 A	04-02-1998
			HU 9802381 A	01-02-1999
			JP 10506956 T	07-07-1998
			NO 974832 A	22-12-1997
			NZ 306894 A	28-07-1998
			PL 322898 A	02-03-1998
WO 9719977	A	05-06-1997	AU 7582896 A	19-06-1997
			EP 0861282 A	02-09-1998
			NO 982433 A	28-07-1998
			US 5864000 A	26-01-1999
DE 1694974	A	26-08-1971	NONE	







## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08G 77/42, C08L 83/10, 61/06</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/40146</b> <b>(43) International Publication Date:</b> 12 August 1999 (12.08.99)
<b>(21) International Application Number:</b> PCT/IB99/00207 <b>(22) International Filing Date:</b> 8 February 1999 (08.02.99) <b>(30) Priority Data:</b> 98420024.6      9 February 1998 (09.02.98)      EP <b>(71) Applicant (for all designated States except US):</b> M3D SOCI- ETE ANONYME [FR/FR]; 16B, rue des Jardins, F-74240 Gaillard (FR). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> KANELLOPOULOS, Vasilios [CH/CH]; 6, chemin Sous-le-Crêt, CH-1256 Troinex (CH). LOUIS-JOSEPH-DOGUE, Isabelle [FR/FR]; 43, rue du Dr Coquand, F-74100 Annemasse (FR). MCGINNISS, Vincent, Daniel [US/US]; P.O. Box 702, Sunbury, OH 43074 (US). MANGARAJ, Duryodhan [US/US]; 7828, Backjack Court, Dublin, OH 43017 (US). NAKAMURA, Tomoki [JP/JP]; Tsuchiya, Narita, Chiba 892-11 (JP). <b>(74) Agents:</b> MOINAS, Michel et al.; Moinas Savoye & Cronin, 42, rue Plantamour, CH-1201 Geneva (CH).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** A POLYMERIC COMPOSITION FOR FRICTION ELEMENTS**(57) Abstract**

The polymeric composition for friction elements comprises a co-polymer between (I) a resin containing phenolic groups and a reticulation agent, and (II) an organopolysiloxane resin containing terminal silanol groups. A part at least of the phenolic groups is bound to the terminal silanol groups. A process of the preparation of the above polymeric composition may comprise the following steps: a) mixing (I) a resin containing the phenolic groups and the reticulation agent, (II) resin containing the terminal silanol groups, and (III) an epoxy resin or the epoxidised organopolysiloxane; b) curing the mixture for a period of time sufficient to complete substantially the reaction between the phenolic groups and the terminal silanol groups, c) post-heating the product obtained under b).

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

## A POLYMERIC COMPOSITION FOR FRICTION ELEMENTS

---

The invention is concerned with a polymeric composition for friction elements having remarkable properties with regard to temperature and contact with water. Although the invention will be described in more details with relation to brake pad or brake linings, it should be understood that it may be used in any application in which friction properties have to remain stable with increasing temperature and with water, such brakes and clutches for vehicles and machine tools. The brake pad is one example in which heat and water are of a prime importance due to a possible overheating if the braking action is applied for an extended period of time, during which moreover water may come in contact with the pads.

Preparations or compositions for friction elements for use in brake pads and other applications are known. One example a is mixture in which a phenolic resin and an organopolysiloxane or silicon resin are mixed with a crosslinking agent and described for instance in EP-0 456 490 and JP-63-251 452.

However, according to IR analysis, this mixture appears to be basically a simple mixture of the original phenolic resin and the product of the homoreaction between the silicon resin and itself. This means in particular that the reaction involved do not lead to specific interactions of the phenolic hydroxy groups with the silicon, most of the phenolic groups remaining as such, i.e as free phenolic groups. Hydrophilic properties are therefore retained together with a relatively high capacity of water absorption, which in turn is affecting strongly the friction characteristics of the product.

The object of the invention is therefore to make the reaction between a phenolic resin and an organopolysiloxane or silicon resin follow a different way, resulting in a actual co-reaction or condensation by co-polymerisation between the phenolic groups and the silanols groups of the silicon in Si-O-C and C-O-C bonds. A part at least of the free phenolic groups of the starting phenolic are consumed in such bonds and will not longer be available for water absorption. The reaction product will loose its hydrophilic properties and the water which may come in contact with said product will not be absorbed, yielding a composition with improved friction properties even under wet conditions.

Another object of the invention is to prepare a composition with superior heat resistance.

Another object of the invention is to prepare a composition with improved wet conditions performance.

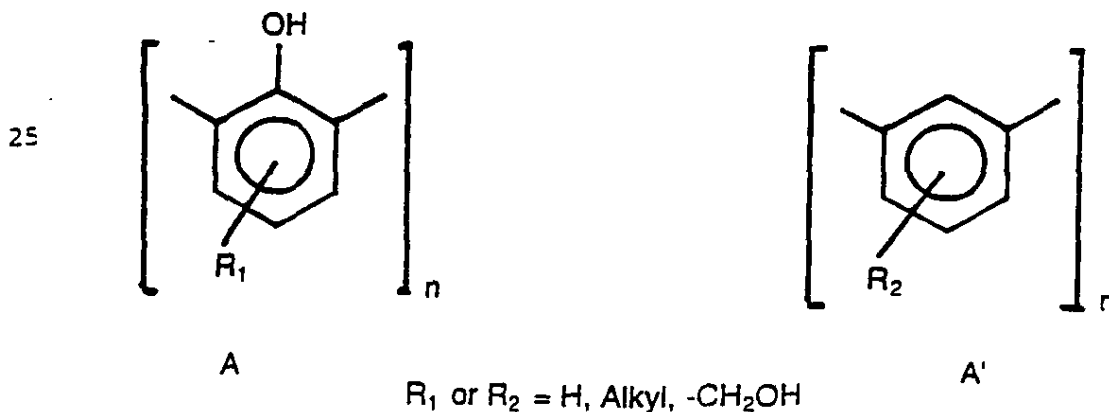
5 In other words, the invention relates to a polymeric composition for friction elements, comprising a co-polymer between (I) a resin containing phenolic groups and a reticulation agent and (II) an organopolysiloxane resin or silicon containing terminal silanol groups, a part of the phenolic groups being bound to the terminal silanol groups.

10 Preferably, the resin containing phenolic groups is from 50 to 80 % and the organopolysiloxane resin containing terminal silanol groups is from 8 to 25 % by weight of the total starting mixture.

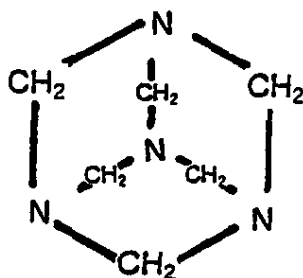
The starting resin comprising phenolic groups may also comprise terminal non aromatic alcoholic groups, a part at least of the terminal non aromatic alcoholic groups being also bound to the terminal silanol groups.

The reticulation agent may be an amine, such as an hexamine.

In one embodiment of the invention, the reticulation agent is an hexamine and is already present as a mix in a resin containing phenolic groups. Such a starting material is for instance that sold under the name of <sup>®</sup>Xylox by Mitsui  
20 Toatsu Chemicals. In this commercial product, the resin containing phenolic groups is of the general formula (A) and may include moieties of a general formula (A'), and contains hexamine (B) in a proportion between 8 and 12 % by weight.



-3-



5

Other starting materials of the same sort may be used as well, such as  
 \*Novalak type of resins

The other compound, namely an organopolysiloxane resin containing  
 10 terminal silanol groups may be an hydroxy phenyl alkyl silicone resin or  
 methyphenylsiloxane for instance.

The invention relates as well to a process for the preparation of the  
 polymeric composition, comprising the following steps :

a) mixing (I) a resin containing the phenolic groups and the reticulation  
 15 agent, (II) a resin containing the terminal silanol groups, and (III) an epoxy resin or  
 the epoxidised organopolysiloxane

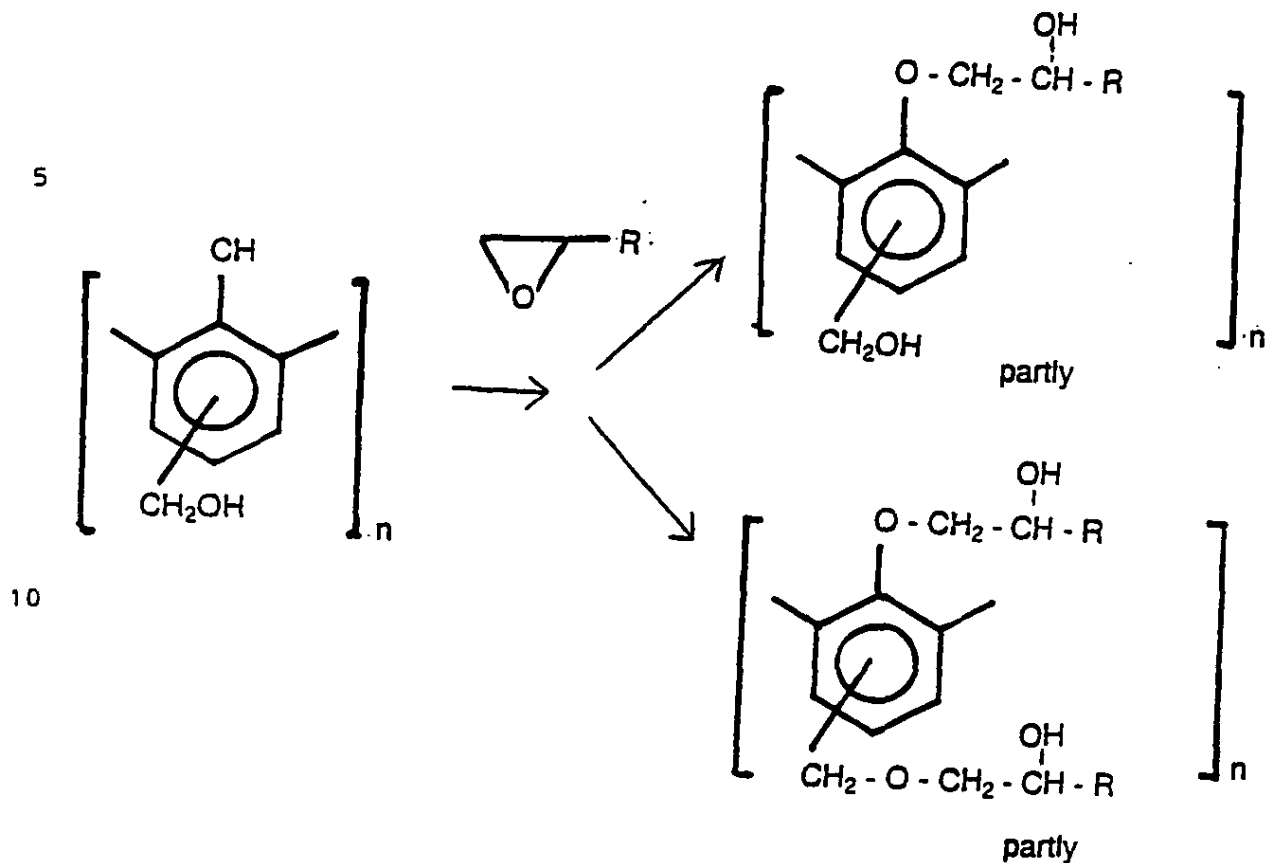
b) curing the mixture for a period of time sufficient to substantially complete  
 the reaction between the phenolic groups and the terminal silanol groups,

c) post-heating the product obtained under b).

20

It should be noted that the reaction is made in the presence of an epoxy  
 resin or an epoxidised organopolysiloxane. This will push the reaction towards the  
 way of a condensation or co-reaction leading to a copolymer rather than a simple  
 homoreaction between the silicone resin and itself as mentioned above for the prior  
 art.

Such a reaction involving the epoxy resin may be symbolised as follows :



15 The silicone resin is present in the starting mixture from 10 to 20 % by weight , preferably around 20%. The epoxy resin may be for instance of <sup>®</sup>Ciba-Geigy (GT 7071) type and may be present in the starting mixture from 20 to 40 % by weight. The epoxidised organopolysiloxane may be for instance a polydialkylsiloxane and may be present in the starting mixture from 3 to 10%, but

20 preferably around 5%

To make easier the blending of the starting resins, said resins are preferably in a form of powder with a particle size distribution of not more than 400  $\mu\text{m}$ , preferably below 300  $\mu\text{m}$  for a compound such as <sup>®</sup>Xylok cited above, and 200  $\mu\text{m}$  for silicone.

25 The mixing step a) which may be held as well as a step for forming or shaping the end product is preferably conducted in a mould at a temperature not exceeding 50°C.

-5-

In general, the curing step b) is conducted under a pressure of at least 50 atm and a temperature from 80 to 160°C and may be divided in a number of cycles permitting the degassing of the reaction mixture. In this case each degassing cycle is most preferably performed in sequence at increasing pressures and temperatures.

As to the post-heating step c) the temperature is advantageously of at least 200°C, under atmospheric pressure.

The various objects and advantages of the invention will become apparent with regard to the following non limitative examples.

#### EXAMPLES 1 TO 7

From a starting blend containing 20% epoxy resin GT 7071, 10% silicone resin 6-2230 and 70%<sup>®</sup>Xylok, samples of 10 x 60 mm (table 1) were fabricated following the conditions described below.

- Step 0: At least 60 s at the curing temperatures without pressure
- Step 1: 5 degassing cycles with a pressure of 146 atm (6 s on, 10 s off) at the curing temperatures for 5, 12, 17.5, 23, or 30 minutes respectively at the curing temperature with a pressure of 183 atm.
- Step 2: 10 minutes at 160°C with 3 degassing cycles (6 s on, 10 s off)

Table 1

Example	Curing temperature (°C)	Time (min)
1	80	23
2	80	12
3	150	23
4	150	12
5	115	5
6	115	30
7	115	17.5

Specimens of these formulations were submitted to different post-curing temperatures of 200°C and 240°C and processed with a brake pad with the usual additional ingredients, to form specific formulations for water tests.

The water absorption was tested using a method, where a 10 µl water drop is deposited at the surface of the sample and the time for absorption is recorded (table 2). On a <sup>®</sup>Teflon surface, which was used as a reference, a 10 µl drop was evaporated in 60 minutes.

Table 2

Examples	Curing Temperature (°C)	Post-curing at 200°C	Post-curing at 240°C
2	80	55 min	61 min
3	115	62 min	74 min
6	150	63 min	67 min

The results showed that the time needed for the water to disappear corresponds to almost that for its evaporation, which confirms that the water absorption for these resin formulations is very low.

After a heat treatment to 350°C, which was intended to simulate heating and over heating by braking, the following comparative results were obtained for formulations post-cured at 240°C.

With specific formulations (resin and other conventional brake pad ingredients) prepared for water tests, the time needed for water to disappear (absorber or evaporated) for pure <sup>®</sup>Xylox correspond to 12 s and to 10s after heating at 350°C for 1h and 2 h respectively. The corresponding times for the specific formulations according to the invention, were at 407 s after 1h heating at 350°C and 186 s after 2h heating at 350°C.

Several reactions could be expected between the different compounds of the formulations:

- the OH end groups of the Xylok could react with the epoxy groups of GT 7071 resin allowing the formation of a C-O-CH<sub>2</sub>-CHOH- bond,

- the OH end groups of the Xylok could react with those of the polydimethyl siloxane 6-2230 leading to the formation of a Si-C-O bond.



-7-

Infra-red vidence of the formation of those groups should be the reduction of the phenyl-CH<sub>2</sub>-OH characteristic band near 1010 cm<sup>-1</sup> as well as the appearance of the typical bands of Si-C-O bond near 1100 cm<sup>-1</sup> (asymmetric stretching vibrations) and C-O-CH<sub>2</sub> bond near 1040 cm<sup>-1</sup>.

- 5 The time and temperature of exposure before curing (step 1) are important to the extent of reaction between silicone-hydroxyl and <sup>®</sup>Xylok-hydroxyl groups. Hence, the change in the peaks were studied as a function of pre-curing temperature and time. Table 3 (reference bands with regards to starting resins) and Table 4 below summarise the characteristic bands for each IR spectrum.

10

Table 3

Bands/ Samples	Epoxy groups 835 cm <sup>-1</sup>	Si-O-C 850 cm <sup>-1</sup>	Si-OH 900 cm <sup>-1</sup>	$\phi$ CH <sub>2</sub> OH 1010 cm <sup>-1</sup>	Si-O-C or C-O-C- 1100 cm <sup>-1</sup>	-C = O 1650 cm <sup>-1</sup>	-CH- 3000 cm <sup>-1</sup>	-OH 3100-3600 cm <sup>-1</sup>
<sup>®</sup> Xylok	none	none	none	strong	weak	none	strong	strong
Silicone resin	none	none	strong	none	strong	none	weak	weak
Epoxy resin	strong	none	none	none	weak	none	strong	weak

15

Table 4 relates to formulations where step 0 was conducted at 80°C, with comparison to samples where step 0 was conducted of 12 min at 80°C , respectively with no curing or post-curing (3rd column in table).

Table 4

Conditions			Epoxy groups	Si-O-C	Si-OH	$\phi$ CH <sub>2</sub> OH	Si-O-C or C-O-C	-C = O	-CH-	-OH
Reaction time	Curing	Post- curing	835 cm <sup>-1</sup>	850 cm <sup>-1</sup>	900 cm <sup>-1</sup>	1010 cm <sup>-1</sup>	1100 cm <sup>-1</sup>	1650 cm <sup>-1</sup>	3000 cm <sup>-1</sup>	3100- 3600 cm <sup>-1</sup>
12 min	no	no	strong	none	weak	strong	strong	none	strong	strong
12 min	no	no	stronger	none	weak	smaller	strong	none	stronger	stronger
12 min	165°C	no	stronger	none	smaller	smaller	stronger	none	strong	lower
12 min	165°C	240°C	stronger	none	smaller	smaller	stronger	strong	strong	strong
23 min	165°C	240°C	stronger	none	smaller	smaller	stronger	stronger	strong	strong

## EXAMPLES 8 TO 14

From a starting blend containing 5% of epoxidised solution of Dow Corning sold under the name of Additive 23, 20% silicone resin 6-2230 and 75%<sup>®</sup>Xylok, 10 x 60 mm samples (table 1) were fabricated following the conditions described below.

Step 0: At least 1.5 min at the curing temperatures without pressure

Step 1: 5 degassing cycles with a pressure of 148 atm (6 s on, 10 s off) at the curing temperatures. 12, 17.5 or 30 minutes at the curing temperature with a pressure of 183 atm.

Step 2: 10 minutes at 160°C with 3 degassing cycles (6 s on, 10 s off)

Table 5

Examples	Curing temperature (°C)	Time (min)
8	140	23
9	140	12
10	160	23
11	160	12
12	150	5
13	150	30
14	150	17.5

Specimens of these formulations were submitted to different post-curing temperatures of 200°C and 240°C and processed with a brake pad with the usual additional ingredients, to form specific formulations for water tests.

The water absorption was again tested as for the formulations of the previous examples 1 to 7 using the above method of water droplet. As a result., the formulations as presented below, showed similar behaviour to that of the previous examples.

Table 6

Examples	Curing Temperature (O°C)	Reaction time (min)	Post-curing at 200°C	Post-curing at 240°C
9	140	12	70 min	72 min
10	150	17.5	80 min	77 min
14	160	23	77 min	66 min

The results showed that the time needed for the water to disappear corresponds to almost that for its evaporation, which confirms that the water absorption for these resin formulations is very low.

After a heat treatment to 350°C, which was intended to simulate heating and over heating by breaking, the following comparative results were obtained for formulations post-cured at 240°C.

With specific formulations (resin and other conventional brake pad ingredients) prepared for water tests, the time needed for water to disappear (absorbed or evaporated) for pure <sup>®</sup>Xylox correspond to 12 s and to 10 s after heating at 350°C for 1h and 2 h respectively. The corresponding times for the specific formulations according to the invention, were 1'972 s after 1 h heating at 350°C and 1'832 s after 2 h heating at 350°C.

Also, if time needed for the water to disappear (absorbed or evaporated) correspond to 100% for the respective above inventive formulations as crude samples (no treatment to 350°C), then after 1 h of heating to 350°C these specific formulations for water tests were at 75 %, 98 % and 98 % respectively for pure <sup>®</sup>Xylox, Mitsui product (<sup>®</sup>Xylox plus Si) and the inventive formulations.

However, after 2 h of heating at 350°C, the results were 63 %, 53 % and 87 % respectively for pure <sup>®</sup>Xylox, Mitsui product (<sup>®</sup>Xylox plus Si) and the inventive formulations.

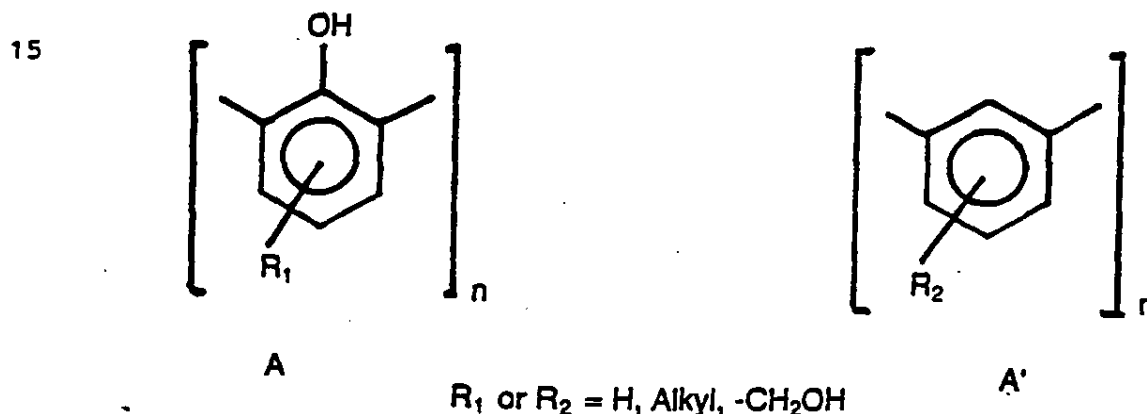
These results indicate the excellent performance and good resistance of the inventive resin formulations to prolonged heat treatments as compared to pure <sup>®</sup>Xylox or even the Mitsui product (<sup>®</sup>Xylox plus Si).

## CLAIMS

1. A polymeric composition for friction elements which comprises a co-polymer between (I) a resin containing phenolic groups and a reticulation agent (II) an organopolysiloxane resin containing terminal silanol group, a part at least of the phenolic groups being bound to the terminal silanol groups, and an epoxy resin or an epoxidised organopolysiloxane (III).

2. A polymeric composition according to claim 1, wherein the resin comprising phenolic group comprises also terminal non aromatic alcoholic groups, a part at least of the terminal non aromatic alcoholic groups being bound to the terminal silanol groups.

3. A polymeric composition according to any of the preceding claims, in which the resin (I) containing phenolic groups is of general formula (A) and may include moieties of the general formula (A') :

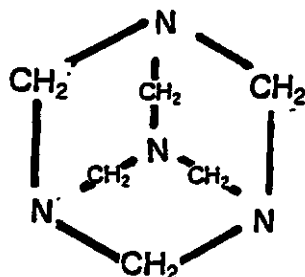


20 4. A polymeric composition according to claim 3, in which the resin (I) containing phenolic groups is of general formula (A) and includes moieties of the general formula (A').

25 5. A polymeric composition according to any of the preceding claims, in which the organopolysiloxane resin (II) containing terminal silanol groups is a hydroxy phenyl alkyl silicone resin.

- 11 -

6. A polymeric composition according to any of the preceding claims, in which the reticulation agent is an hexamine of general formula (B) :



7. A process of preparation of a polymeric composition according to any of the preceding claims, comprising the following steps :

a) mixing (I) a resin containing the phenolic groups and the reticulation agent, (II) resin containing the terminal silanol groups, and (III) an epoxy resin or the epoxidised organopolysiloxane

b) curing the mixture for a period of time sufficient to complete substantially the reaction between the phenolic groups and the terminal silanol groups,

c) post-heating the product obtained under b).

8. A process according to claim 7. in which the mixing step a) is conducted at a temperature not exceeding 50°C.

9. A process according to claim 8, in which the curing step b) is conducted under a pressure of at least 50

atm and the temperature is from 80 to 160°C.

10. A process according to claim 7. in which the curing step b) is divided in a number of cycles permitting the degassing of the reaction mixture.

11. A process according to claim 10, in which each degassing cycle is conducted in sequence at increasing pressure and temperature.

12. A process according to claim 7 in which the post-heating step c) is conducted at a temperature of at least 200°C under atmospheric pressure.

13. A process according to claim 7 in which the starting resins are in a form of powder with a particle size distribution of not more than 400  $\mu\text{m}$
14. The use of the polymeric composition of any of claims 1 to 6 as a substrate for brake pads

## INTERNATIONAL SEARCH REPORT

Internat al Application No

PCT/IB 99/00207

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G77/42 C08L83/10 C08L61/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 657 951 A (TAKARADA MITSUHIRO ET AL) 14 April 1987 see claims 1-6 ---	1,2,4-6, 14
X	US 3 911 045 A (HARTMANN PETER ET AL) 7 October 1975 see claim 1 see column 2, line 33 - line 60 ---	1
X	WO 96 33238 A (AMERON INC ;KANE JOHN F (US); MOWRER NORMAN R (US)) 24 October 1996 see claims 1-43 see page 3, line 3 - line 4 see page 16, line 16 - line 31 see page 36, line 25 - line 30 --- -/-	1,2,4-6

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Z" document member of the same patent family

Date of the actual completion of the international search

21 April 1999

Date of mailing of the international search report

04/05/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
3100

Authorized officer

Depijper, R

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 19977 A (BP CHEM INT LTD) 5 June 1997 see claims 1-10	1
X	DE 16 94 974 A (STENBECK G) 26 August 1971 see claim 1 see page 1, paragraph 3 see page 3; example 1	1



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 99/00207

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4657951 A	14-04-1987	JP 2015978 C	19-02-1996
		JP 6092524 B	16-11-1994
		JP 61192711 A	27-08-1986
US 3911045 A	07-10-1975	DE 2306463 A	29-08-1974
		AU 476576 B	30-09-1976
		AU 6525674 A	07-08-1975
		BE 810720 A	07-08-1974
		CA 1033491 A	20-06-1978
		CS 175473 B	31-05-1977
		DD 111395 A	12-02-1975
		FR 2217376 A	06-09-1974
		GB 1424290 A	11-02-1976
		JP 1047903 C	28-05-1981
		JP 49113000 A	28-10-1974
		JP 55039183 B	08-10-1980
		NL 7401649 A	13-08-1974
		ZA 7400835 A	24-12-1974
WO 9633238 A	24-10-1996	US 5736619 A	07-04-1998
		AU 699446 B	03-12-1998
		AU 5558396 A	07-11-1996
		BR 9608196 A	21-07-1998
		CA 2218694 A	24-10-1996
		CZ 9703331 A	17-06-1998
		EP 0821711 A	04-02-1998
		HU 9802381 A	01-02-1999
		JP 10506956 T	07-07-1998
		NO 974832 A	22-12-1997
		NZ 306894 A	28-07-1998
		PL 322898 A	02-03-1998
WO 9719977 A	05-06-1997	AU 7582896 A	19-06-1997
		EP 0861282 A	02-09-1998
		NO 982433 A	28-07-1998
		US 5864000 A	26-01-1999
DE 1694974 A	26-08-1971	NONE	



## PATENT COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

MOINAS, Michel  
Moinas Savoye & Cronin  
42, rue Plantamour  
CH-1201 Geneva  
SUISSE

Date of mailing (day/month/year) 03 July 2000 (03.07.00)	<b>IMPORTANT NOTIFICATION</b>
Applicant's or agent's file reference M150/WO/005	
International application No. PCT/IB99/00207	International filing date (day/month/year) 08 February 1999 (08.02.99)

## 1. The following indications appeared on record concerning:

☒ the applicant    ☐ the inventor    ☐ the agent    ☐ the common representative

Name and Address M3D SOCIETE ANONYME 16B, rue des Jardins F-74240 Gaillard France	State of Nationality FR	State of Residence FR
	Telephone No. +33 4 5043 2000	
	Facsimile No. +33 4 5043 2001	
	Teleprinter No.	

## 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☒ the person    ☒ the name    ☒ the address    ☐ the nationality    ☐ the residence

Name and Address NISSHINBO INDUSTRIES, INC. 31-11, Nihonbashi Ningyocho 2-chome Chuo-ku Tokyo 103-8650 Japan	State of Nationality JP	State of Residence JP
	Telephone No.	
	Facsimile No.	
	Teleprinter No.	

## 3. Further observations, if necessary:

Please be informed that a power of attorney is still missing.

## 4. A copy of this notification has been sent to:

<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned
<input type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer  Christine Carrié
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38



# PATENT COOPERATION TREATY

## PCT

### NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C. 20231  
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

<b>Date of mailing (day/month/year)</b> 29 October 1999 (29.10.99)	
<b>International application No.</b> PCT/IB99/00207	<b>Applicant's or agent's file reference</b> M150/WO/005
<b>International filing date (day/month/year)</b> 08 February 1999 (08.02.99)	<b>Priority date (day/month/year)</b> 09 February 1998 (09.02.98)
<b>Applicant</b> KANELLOPOULOS, Vasilios et al	

1. The designated Office is hereby notified of its election made:



in the demand filed with the International Preliminary Examining Authority on:

03 September 1999 (03.09.99)



in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

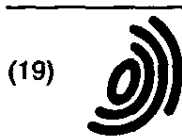


was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland  Facsimile No.: (41-22) 740.14.35	<b>Authorized officer</b>  <p style="text-align: center;">S. Mafla</p> Telephone No.: (41-22) 338.83.38
--	---





Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11) **EP 1 074 573 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
07.02.2001 Bulletin 2001/06

(51) Int Cl.7: **C08G 77/42, C08L 83/10,**  
**C08L 61/06, F16D 69/02**

(21) Application number: **99810697.5**

(22) Date of filing: **04.08.1999**

*too late*

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU**  
**MC NL PT SE**  
Designated Extension States:  
**AL LT LV MK RO SI**

(71) Applicant: **Nisshinbo Industries, Inc.**  
**Chuo-ku, Tokyo 103-8650 (JP)**

(72) Inventors:  
• **Kanellopoulos, Vasilios**  
**1256 Troinex (CH)**

- **Louis-Joseph-Dogue-Redon, Isabelle**  
**Sako, Nagano 385003 (JP)**
- **McGinniss, Vincent Daniel**  
**Sunbury, Ohio 43074 (US)**
- **Mangaraj, Duryodhan**  
**Dublin, Ohio 43017 (US)**
- **Nakamura, Tomoki**  
**Narita, Chiba (JP)**

(74) Representative: **Savoye, Jean-Paul et al**  
**Moinas Savoye & Cronin,**  
**42, rue Plantamour**  
**1201 Genève (CH)**

(54) **A polymeric composition for friction elements**

(57) The polymeric composition for friction elements comprises a co-polymer between (I) a resin containing phenolic groups, (II) an organopolysiloxane resin containing terminal silanol groups. A part at least of the phenolic groups is bound to the terminal silanol groups. A tris neoalkalanate titanate is used as a catalyst for the co-polymerisation reaction

A process of the preparation of the polymeric composition comprises the following steps:

a) mixing (I) a resin containing the phenolic groups, (II) a resin containing the terminal silanol groups, and (III) a tris neoalkalanate titanate as a catalyst,

b) curing the mixture for a period of time sufficient to complete substantially the reaction between the phenolic groups and the terminal silanol groups,

c) post-curing the product obtained under b).

*priority ?*





## Description

[0001] The invention is concerned with a polymeric composition for friction elements having remarkable properties with regard to temperature and contact with water. Although the invention will be described in more details with relation to brake pad or brake linings, it should be understood that it may be used in any application in which friction properties have to remain stable with increasing temperature and under wet conditions, such as brakes and clutches for vehicles and machine tools. The brake pad is one example in which heat and water are of a prime importance due to a possible overheating if the braking action is applied for an extended period of time, during which moreover water may come in contact with the pads.

[0002] Preparations or compositions for friction elements for use in brake pads and other applications are known. One example is a mixture in which a phenolic resin and an organopolysiloxane or silicone resin are mixed with a crosslinking agent as described for instance in EP-0 456 490 and JP-63-251 452.

[0003] In the former document a catalyst is used during the preparation, which consists of an organic compound conventionally used in the manufacturing of silicone rubber, such as stannous oleate and tin naphthenate.

[0004] US-4 657 951 is citing other organic metallic salts which can be employed as catalysts in the transesterification between a phenolic resin and an organopolysiloxane. Tetrabutyl titanate, tetra isopropyl titanate and butyl polytitanate are mentioned among others. Zirconates are also known as catalysts for transesterification.

[0005] However, according to IR analysis, this mixture appears to be basically a simple mixture of the original phenolic resin and the product of the homoreaction between the silicone resin and itself. This means in particular that the reaction involved do not lead to specific interactions of the phenolic hydroxy groups with the silicone, most of the phenolic groups remaining as such, i.e. as free phenolic groups. Hydrophilic properties are therefore retained together with a relatively high capacity of water absorption, which in turn is affecting strongly the friction characteristics of the product.

[0006] In our co-pending unpublished European patent application no 98420024.6, an improved polymeric composition for friction elements is disclosed, which comprises a co-polymer between (I) a resin containing phenolic groups and (II) an organopolysiloxane resin or silicone containing terminal silanol groups, a part of the phenolic groups being bound to the terminal silanol groups. Preferably, the reaction between (I) and (II) is made in the presence of an epoxy resin or an epoxidised organopolysiloxane.

[0007] As in the above document, the object of the invention is also to make the reaction between a phenolic resin and an organopolysiloxane or silicone resin follow a different way, resulting in a actual co-reaction or condensation between the phenolic groups and the silanols groups of the silicone in Si-O-C and C-O-C bonds. A part at least of the free phenolic groups of the starting phenolic are consumed in such bonds and will not longer be available for water absorption. The reaction product will loose its hydrophilic properties and the water which may come in contact with said product will not be absorbed, yielding a composition with improved friction properties even under wet conditions.

[0008] An object of the invention is products which exhibit still improved properties over the products just mentioned above in the unpublished European Patent Application.

[0009] Another object of the invention is to prepare a composition with superior heat resistance.

[0010] Another object of the invention is to prepare a composition with improved wet conditions performance.

[0011] In other words, the invention relates to a polymeric composition for friction elements, comprising a co-polymer between (I) a resin containing phenolic groups, (II) an organopolysiloxane resin or silicone containing terminal silanol groups and (III) a reticulation agent, a part at least of the phenolic groups being bound to the terminal silanol groups, wherein tris neoalkalanate titanate is used as a catalyst for the co-polymerisation reaction.

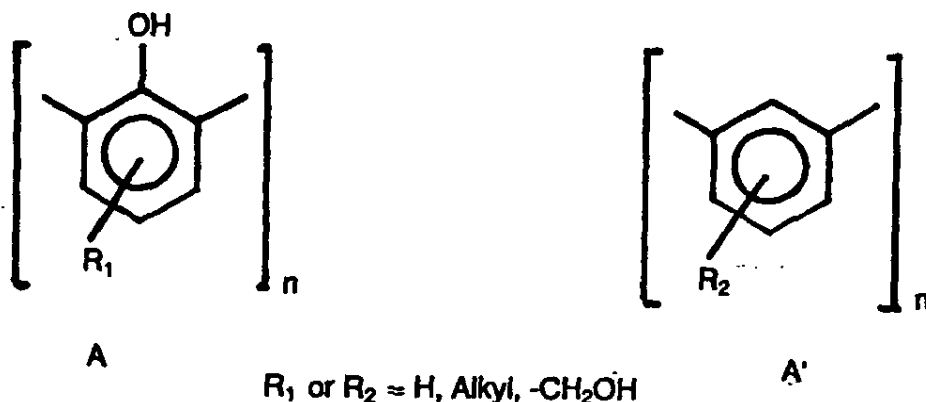
[0012] Preferably, the resin containing phenolic groups is from 50 to 80 % and the organopolysiloxane resin containing terminal silanol groups is from 8 to 25 % by weight of the total starting mixture.

[0013] The starting resin comprising phenolic groups may also comprise terminal non aromatic alcoholic groups, a part at least of the terminal non aromatic alcoholic groups being also bound to the terminal silanol groups.

[0014] The reticulation agent may be an amine such as an hexamine, preferably to the extend of 8 to 12 % by weight.

[0015] In one embodiment, the resin containing phenolic groups is of the general formula (A) and may include moieties of a general formula (A').





[0016] A typical convenient resin is for instance a phenyl aralkyl resin in which  $R_1$  is  $-\text{CH}_2-\phi-$  having a basic structure of alternated moieties A/A'. A variety of such resins are sold under the generic name of  $\text{Xylok}$  by Mitsui Toatsu Chemical, Japan.

[0017] The other compound, namely an organopolysiloxane resin containing terminal silanol groups may be for instance a diphenyl silicone or an hydroxy phenyl alkyl silicone resin or methyphenylsiloxane.

[0018] Among tris neoalkalanate titanates, those neoalkalanates having between 2 and 16 C atoms on each chain, saturated or unsaturated, unbranched or branched, are preferred. These titanates may contain hetero-atoms atoms or heterocyclic moieties.

[0019] Examples of convenient catalysts within the above definition are :

- neopentyl (diallyl)oxy tridecanoyl titanate,
- neopentyl (diallyl) oxy tri(didecyl)benzenesulfonyl titanate,
- neopentyl (diallyl) oxy tri(dioctyl)phosphato titanate,
- neopentyl (diallyl) oxy tri(dioctyl)pyrophosphate titanate,
- their adducts with acrylate and methacrylate functional amines,
- neopentyl (diallyl)oxy tri(N-ethylenediamino) ethyl titanate,
- neopentyl (diallyl) oxy tri(m-amino)phenyl titanate,
- neopentyl (diallyl)oxy trihydroxy caproyl titanate,

all sold by Kenrich Petrochemical under the general name of  $\text{Lica}$ . A preferred catalyst is neopentyl (diallyl) oxy trineodecanoyl titanate.

[0020] The invention relates as well to a process for the preparation of the polymeric composition, comprising the following steps :

- a) mixing and kneading together (I) a resin containing the phenolic groups with (II) a resin containing the terminal silanol groups, in the presence of a tris neoalkalanate titanate as a catalyst, for a period of time sufficient to substantially complete the reaction between the phenolic groups and the terminal silanol groups, to yield a paste,
- b) cooling down the paste until obtaining a solid,
- c) grinding the solid into a powder,
- d) adding the reticulation agent to said powder,



e) curing the above mixture,

f) post-curing the product obtained under e).

[0021] In the above processes, the catalyst tris neoalkalanate titanate is preferably used in quantities comprised between 1 and 2 % by weight of the total mixture.

[0022] If the co-polymerisation reaction is conducted in solution, then the catalyst may be present in higher quantities, preferably between 1 and 18 % by weight of the total mixture.

[0023] Due to the high efficiency of the reaction in condensing the phenolic groups with the terminal silanol groups, such a reaction may be described as "end capping".

[0024] The silicone resin is present in the starting mixture from 8 to 25 % by weight, preferably around 10 to 20%. Si 6-2230 (a diphenylsilicone) of @Dow Corning Silicone, Z-6018 (an other diphenyl silicone) of @Dow Corning or PDS 9931 (an other diphenyl silicone) of @Gelest Inc. are examples of such silicone resins.

[0025] To make easier the blending of the starting resins, said resins are preferably in a form of powder with a particle size distribution of not more than 400  $\mu\text{m}$ , preferably below 300  $\mu\text{m}$  for a compound such as @Xylok cited above, and 200  $\mu\text{m}$  for silicone.

[0026] The mixing and kneading under step a) of the resins and the catalyst, said catalyst having the consistency of honey, is preferably conducted in a vessel at a temperature of 80 to 135°C under a nitrogen pressure of 1 to 2 atm. This is easily carried out in a kneading machine with a rotation speed between 30 and 80 rpm.

[0027] The paste obtained above is then cooled or chilled down, for instance simply by leaving it at room temperature for a sufficient period of time. When solid, it is ground to yield a powder with a particle size distribution advantageously between 10 and 200  $\mu\text{m}$ .

[0028] The hexamine is then added and throughoutly mixed to the powder, and the mixture is cured at a temperature between 50 to 200 °C, for instance around 170-180°C, under a pressure of 250 to 320 atm.

[0029] In general, the curing step is divided in a number of cycles (5 to 20 cycles for instance) permitting the degassing of the reaction mixture.

[0030] As to the post-curing, the heating temperature is advantageously from 190 to 240°C.

[0031] The various objects and advantages of the invention will become apparent with regard to the following non limitative examples.

### EXAMPLES 1 TO 3

[0032] From a starting blend containing a silicone resin of different types according to the examples, a @Xylok free of reticulation agent (available by Mitsui Chemicals, Japan), and 1,4 % of neopentyl (diallyl) oxy trineodecanonyl titanate (@Lica-01 of Kenrich Petrochemicals), samples of the following table 1 were fabricated using the parameters given above and in the following additional conditions :

10 degassing cycles with a pressure of 300 atm (6 seconds on, 4 seconds off) at 175°C.

Post-curing during 10 minutes at 200°C

Table 1

Example	Compositions	
1	Si-62230	24.25%
	Xylok	74.35%
	Lica-01	1.4%
2	Z-6018	19.5%
	Xylok	79.1%
	Lica-01	1.4%
3	PDS 9931	20.0%
	Xylok	78.6 %
	Lica-01	1.4%

[0033] Specimens of these formulations were used as a substrate or binder to be processed into a "simplified" brake pad sample with a minimum number of ingredients, to form specific formulations for water tests. "Simplified" brake pad



is intended to designate a model or simulation probe for tests traditionally made by using a simplified mix of 4 components only, whereas an actual brake pad for vehicles is a more complex mixture of over 15 ingredients.

[0034] The water absorption was tested using a method, where a 10  $\mu$ l water drop is deposited at the surface of the sample and the time for absorption is recorded. On a @Teflon surface, which was used as a reference, a 10  $\mu$ l drop disappeared in 60 minutes.

[0035] The droplet on a pad surface having a composition corresponding to example 1 disappeared in 60 minutes when said pad has not been heated, and in 57 minutes when the pad has been submitted to a heating cycle at 350°C during 1 hr. These values indicate no water affinity, very near to that of @Teflon, and an excellent resistance to heating and overheating.

#### COMPARATIVE EXAMPLE

[0036] By way of comparison, a comparative formulation corresponding to examples 1,2 and 3 was made by the same procedure, but without using the silicone resin and the catalyst, in order to demonstrate the effect of the "end capping". All formulations of examples 1 to 3 and of the comparative example were submitted to a heat treatment simulating heating and over-heating due to a braking action. A temperature of 350°C was used for 1 hr and 2 hr receptively. Results of the above "droplets" tests, expressed in minutes, are given below in Table 2 :

Table 2

	1	2	3	comparative formulation
non heated	66	64	60	37
heated 350°C/1h	57	54	48	12
heated 350°C/2 hr	16	14	17	8

[0037] Conclusions are clear. Formulations of examples 1 to 3 are far superior to the comparative formulation prepared without the tris neoalkalanate titanate catalyst. Times to absorb water are at least twice as much. The peak of almost 5 times (57, resp. 54, resp. 48 vs 12) for a heat treatment of 1 hr is of a prime importance, since it is a more realistic time for an excessive braking action (descending under full load conditions).

[0038] Another comparison between Example 1 and the same comparative formulation is given below in Table 3. This time, test samples are actual brake pads using all the traditional ingredients.

Table 3

		example 1	comparative formulation
Water absorption in minutes	non heated	40	44
	heated 350°C/1hr	35	28
	heated 350°C/2 hr	17	9
Bending strength in kgf/mm <sup>2</sup>	non heated	3,87	3,99
	heated 350°C/1hr	2,15	1,41
	heated 350°C/2 hr	1,80	1,12

[0039] Again resistance to water and mechanical properties, although comparable before heat treatment, are far better after heat treatment.

#### EXAMPLES 4 AND 5

[0040] The following products of examples 4 and 5 were prepared in solution , as follows :

[0041] Ex. 4 : 3/7 of @Xylok, 3/7 of silicone resin Si 62230 and 1/7 of neopentyl (diallyl)oxy tridecanoyl titanate (@Lica-01) as a catalyst by weight were mixed for 2 hr at 155-160°C.

[0042] Ex. 5 : 3/7 @Xylok, 3/7 of silicone resin Z-6018 and 1/7 of neopentyl (diallyl)oxy tridecanoyl titanate (@Lica-01) as a catalyst by weight were mixed for 2 hr at 155-160°C.

#### COMPARATIVE EXAMPLES

[0043] For comparison purposes, the following products were prepared in solution in DMF, as described above :

[0044] Comp. Ex 4 : @Xylok (3/7 by weight), silicone resin Si 62230 (3/7 by weight) and tetra isopropyl titanate (1/7





by weight) of the art (as mentioned above) as a catalyst by weight were mixed during 2 hr at 155-160°C. Tetra isopropyl titanate was @Tysor R TPT made by @DuPont Chemicals.

[0045] Comp. Ex. 5 : @Xylok (3/7 by weight), silicone resin Z-6018 (3/7 by weight) and tetra isopropyl titanate (1/7 by weight) of the art as a catalyst by weight were mixed during 2 hr at 155-160°C. Tetra isopropyl titanate was also @Tysor R TPT made by @DuPont Chemicals.

[0046] All above products of examples 4 and 5, and of the comparative examples, were examined by ultra violet spectroscopy after addition of a small amount of KOH in order to ionise the phenolic groups, which show absorption at 280 and 275 nm. Results are given below, in Table 4.

Table 4

examples	280 nm	275 nm
4	no peak	no peak
5	no peak	no peak
Comparative 4	1,84	1,94
Comparative 5	2,24	2,27

[0047] As seen from Table 4, the products made with the tris neo alkanate titanate catalyst did not show any peak at both wavelengths responsible for phenolic OH absorption. It should be noted that the catalysts were used in amounts in the range of 10 to 15 times of what is needed according to the invention. Even with such concentrations of catalyst in the starting mixtures, the product obtained by using tetra isopropyl titanate as a catalyst did exhibit absorption of phenolic groups.

#### OTHER COMPARATIVE EXAMPLES

[0048] A solution of 7.5 g of @Xylok and 7.5 g of silicone resin and no catalyst, respectively 2 g of nonaloxo zirconate as a catalyst, was mixed for two and four hours.

[0049] The product was examined by ultra violet spectrophotometry after the addition of a small amount of KOH in order to ionise the phenolic groups (see Table 5).

[0050] The ionised phenolic groups show absorption at 280 and 275 nm.

[0051] When reaction occurs between @Xylok and silicone, no ionised phenolic groups appear after addition of KOH.

Table 5

Catalyst	reaction time			
	2 hours		4 hours	
	Abs 280nm	Abs 275 nm	Abs 280nm	Abs 275 nm
no catalyst	1.2	1.3	1.2	1.3
nonaloxo zirconate	1.2	1.2	1.3	1.3

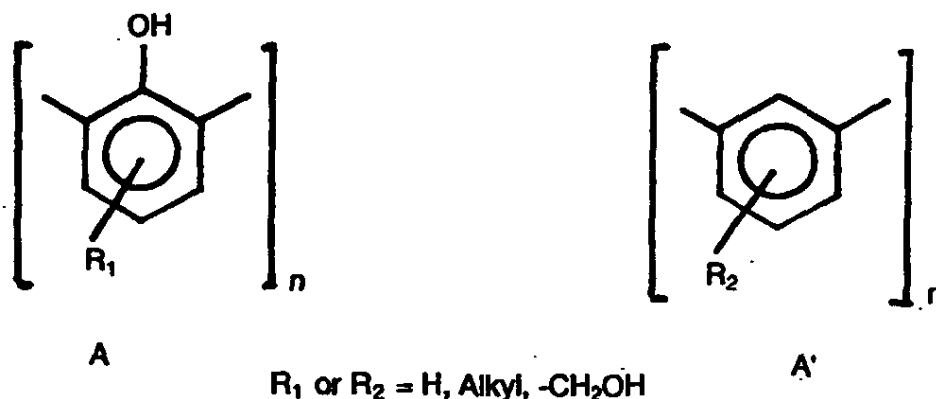
[0052] The use of nonaloxo zirconate leads to results comparable to those obtained without a catalyst and both yields to products having a substantial amount of remaining free phenolic groups.

#### Claims

1. A polymeric composition for friction elements, comprising a co-polymer between (I) a resin containing phenolic groups, (II) an organopolysiloxane resin containing terminal silanol groups, a part at least of the phenolic groups being bound to the terminal silanol groups, wherein tris neoalkalanate titanate is used as a catalyst for the co-polymerisation reaction.
2. A polymeric composition according to claim 1, wherein the resin comprising phenolic group comprises also terminal non aromatic alcoholic groups, a part at least of the terminal non aromatic alcoholic groups being bound to the terminal silanol groups.



3. A polymeric composition according to any of the preceding claims, in which the resin (I) containing phenolic groups is of general formula (A) and may include moieties of the general formula (A'):



- 20
4. A polymeric composition according to claim 3, wherein the resin comprising phenolic group is a phenyl aralkyl resin having a basic structure of alternated moieties A/A'.
- 25
5. A polymeric composition according to any of the preceding claims, in which the resin containing phenolic groups is from 50 to 80 % and the organopolysiloxane resin containing terminal silanol groups is from 8 to 25 % by weight of the total starting mixture.
- 30
6. A polymeric composition according to any of the preceding claims, in which the organopolysiloxane resin (II) containing terminal silanol groups is a diphenyl silicone or a hydroxy phenyl alkyl silicone resin.
7. A polymeric composition according to claim 1, in which the reticulation agent is an amine such as hexamine.
- 35
8. A polymeric composition according to claim 1, in which the catalyst is neopentyl (diallyl) oxy trineodecanonyl titanate
9. A process of preparation of a polymeric composition according to any of the preceding claims, comprising the following steps :
- 40
- a) mixing and kneading together (I) a resin containing the phenolic groups with (II) a resin containing the terminal silanol groups, in the presence of a tris neoalkalanate titanate as a catalyst, for a period of time sufficient to substantially complete the reaction between the phenolic groups and the terminal silanol groups, to yield a paste,
- 45
- b) cooling down the paste until obtaining a solid,
- c) grinding the solid into a powder,
- 50
- d) adding the reticulation agent to said powder,
- e) curing the above mixture,
- f) post-curing the product obtained under e)
10. A process according to claim 9, in which the tris neoalkalanate titanate is used in quantities comprised between 1 and 2 % by weight of the total mixture.
- 55
11. A process according to claim 9 or 10 in which the curing step is divided in a number of cycles permitting the degassing of the reaction mixture.
12. A process according to claim 9 or 10 in which the starting resins are in a form of powder with a particle size



**EP 1 074 573 A1**

distribution of not more than 400  $\mu\text{m}$ .

**13.** The use of the polymeric composition of any of claims 1 to 7 as a binder for brake pads

5

10

15

20

25

30

35

40

45

50

55





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 99 81 0697

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
E,D	EP 0 934 967 A (M3D) 11 August 1999 (1999-08-11) * the whole document *	1-3,5,6, 11-13	C08G77/42 C08L83/10 C08L61/06 F16D69/02
X	WO 96 33238 A (AMERON INC ;KANE JOHN F (US); MOWRER NORMAN R (US)) 24 October 1996 (1996-10-24) * page 3, line 1 - line 20 * * page 16, line 16 - page 17, line 5 * * page 17, line 24 - line 30 * * page 36, line 25 - line 30 *	1-3,6,13	
A		8	
X	US 4 657 951 A (M.TAKARADA) 14 April 1987 (1987-04-14) * column 2, line 26 - column 3, line 18 * * column 4, line 5 - line 61 *	1-3,6,13	
Y	US 3 911 045 A (HARTMANN PETER ET AL) 7 October 1975 (1975-10-07) * column 1, line 40 - column 2, line 60 * * column 4, line 13 - line 18 *	1,13	
Y	DE 16 94 974 A (STENBECK G) 26 August 1971 (1971-08-26) * page 1, paragraph 3 * * page 2, line 10 - line 18 *	1,13	F16D C08G C08L
A	WO 97 19977 A (BP CHEM INT LTD) 5 June 1997 (1997-06-05) * page 3, line 1 - line 10 * * page 4, line 11 - line 21; claims 1-10 *	1	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 December 1999	Examiner Boulon, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons Δ : member of the same patent family, corresponding document</p>			





**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 81 0697

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

17-12-1999

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 934967	A	11-08-1999	WO 9940146 A	12-08-1999
WO 9633238	A	24-10-1996	US 5736619 A	07-04-1998
			AU 699446 B	03-12-1998
			AU 5558396 A	07-11-1996
			BR 9608196 A	21-07-1998
			CA 2218694 A	24-10-1996
			CZ 9703331 A	17-06-1998
			EP 0821711 A	04-02-1998
			HU 9802381 A	01-02-1999
			JP 10506956 T	07-07-1998
			NO 974832 A	22-12-1997
			NZ 306894 A	28-07-1998
			PL 322898 A	02-03-1998
US 4657951	A	14-04-1987	JP 2015978 C	19-02-1996
			JP 6092524 B	16-11-1994
			JP 61192711 A	27-08-1986
US 3911045	A	07-10-1975	DE 2306463 A	29-08-1974
			AU 476576 B	30-09-1976
			AU 6525674 A	07-08-1975
			BE 810720 A	07-08-1974
			CA 1033491 A	20-06-1978
			CS 175473 B	31-05-1977
			DD 111395 A	12-02-1975
			ES 423053 A	01-05-1976
			FR 2217376 A	06-09-1974
			GB 1424290 A	11-02-1976
			HU 166676 B	28-05-1975
			JP 1047903 C	28-05-1981
			JP 49113000 A	28-10-1974
			JP 55039183 B	08-10-1980
			NL 7401649 A	13-08-1974
			RO 69129 A	29-04-1983
			ZA 7400835 A	24-12-1974
DE 1694974	A	26-08-1971	NONE	
WO 9719977	A	05-06-1997	AU 7582896 A	19-06-1997
			EP 0861282 A	02-09-1998
			NO 982433 A	28-07-1998
			US 5864000 A	26-01-1999





Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) **EP 0 934 967 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
11.08.1999 Bulletin 1999/32

(51) Int. Cl.<sup>6</sup>: **C08G 77/42**, **C08L 83/10**,  
**C08L 61/06**

(21) Application number: **98420024.6**

(22) Date of filing: **09.02.1998**

(84) Designated Contracting States:  
**AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE**  
Designated Extension States:  
**AL LT LV MK RO SI**

(71) Applicant: **M3D Société Anonyme**  
**74240 Gaillard (FR)**

(72) Inventors:  
• **Kannelopoulos, Vasilios**  
**1256 Troinex (CH)**

• **Louis-Joseph-Dogue, Isabelle**  
**74100 Annemasse (FR)**  
• **McGinniss, Vincent Daniel**  
**Sunbury, Ohio 43074 (US)**  
• **Mangaraj, Duryodhan**  
**Dublin, Ohio 43017 (US)**  
• **Nakamura, Tomoki**  
**Narita, Chiba (JP)**

(74) Representative: **Moinas, Michel**  
**MOINAS SAVOYE & CRONIN,**  
**42 rue Plantamour**  
**1201 Genève (CH)**

(54) **A polymeric composition for friction elements**

(57) The polymeric composition for friction elements comprises a co-polymer between (I) a resin containing phenolic groups and a reticulation agent, and (II) an organopolysiloxane resin containing terminal silanol groups. A part at least of the phenolic groups is bound to the terminal silanol groups.

A process of the preparation of the above polymeric composition may comprise the following steps:

a) mixing (I) a resin containing the phenolic groups and the reticulation agent, (II) resin containing the terminal silanol groups, and (III) an epoxy resin or the epoxidised organopolysiloxane

b) curing the mixture for a period of time sufficient to complete substantially the reaction between the phenolic groups and the terminal silanol groups,

c) post-heating the product obtained under b).

*priority*



## Description

[0001] The invention is concerned with a polymeric composition for friction elements having remarkable properties with regard to temperature and contact with water. Although the invention will be described in more details with relation to brake pad or brake linings, it should be understood that it may be used in any application in which friction properties have to remain stable with increasing temperature and with water, such brakes and clutches for vehicles and machine tools. The brake pad is one example in which heat and water are of a prime importance due to a possible overheating if the braking action is applied for an extended period of time, during which moreover water may come in contact with the pads.

[0002] Preparations or compositions for friction elements for use in brake pads and other applications are known. One example is a mixture in which a phenolic resin and an organopolysiloxane or silicon resin are mixed with a crosslinking agent and described for instance in EP-0 456 490 and JP-63-251 452.

[0003] However, according to IR analysis, this mixture appears to be basically a simple mixture of the original phenolic resin and the product of the homoreaction between the silicon resin and itself. This means in particular that the reaction involved do not lead to specific interactions of the phenolic hydroxy groups with the silicon, most of the phenolic groups remaining as such, i.e. as free phenolic groups. Hydrophilic properties are therefore retained together with a relatively high capacity of water absorption, which in turn is affecting strongly the friction characteristics of the product.

[0004] The object of the invention is therefore to make the reaction between a phenolic resin and an organopolysiloxane or silicon resin follow a different way, resulting in a actual co-reaction or condensation by co-polymerisation between the phenolic groups and the silanol groups of the silicon in Si-O-C and C-O-C bonds. A part at least of the free phenolic groups of the starting phenolic are consumed in such bonds and will not longer be available for water absorption. The reaction product will lose its hydrophilic properties and the water which may come in contact with said product will not be absorbed, yielding a composition with improved friction properties even under wet conditions.

[0005] Another object of the invention is to prepare a composition with superior heat resistance.

[0006] Another object of the invention is to prepare a composition with improved wet conditions performance.

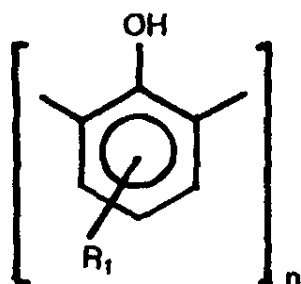
[0007] In other words, the invention relates to a polymeric composition for friction elements, comprising a co-polymer between (I) a resin containing phenolic groups and a reticulation agent and (II) an organopolysiloxane resin or silicon containing terminal silanol groups, a part of the phenolic groups being bound to the terminal silanol groups.

[0008] Preferably, the resin containing phenolic groups is from 50 to 80 % and the organopolysiloxane resin containing terminal silanol groups is from 8 to 25 % by weight of the total starting mixture.

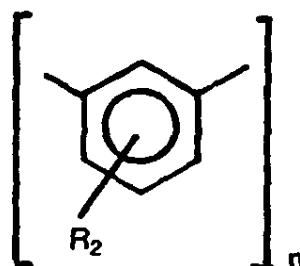
[0009] The starting resin comprising phenolic groups may also comprise terminal non aromatic alcoholic groups, a part at least of the terminal non aromatic alcoholic groups being also bound to the terminal silanol groups.

[0010] The reticulation agent may be an amine, such as an hexamine.

[0011] In one embodiment of the invention, the reticulation agent is an hexamine and is already present as a mix in a resin containing phenolic groups. Such a starting material is for instance that sold under the name of <sup>®</sup>Xylox by Mitsui Toatsu Chemicals. In this commercial product, the resin containing phenolic groups is of the general formula (A) and may include moieties of a general formula (A'), and contains hexamine (B) in a proportion between 8 and 12 % by weight.



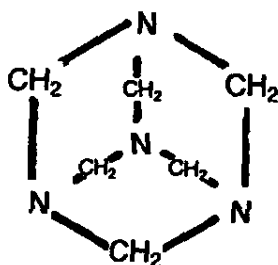
A



A'

$R_1$  or  $R_2 = H, \text{ Alkyl}, -CH_2OH$





[0012] Other starting materials of the same sort may be used as well, such as <sup>®</sup>Novalak type of resins

[0013] The other compound, namely an organopolysiloxane resin containing terminal silanol groups may be an hydroxy phenyl alkyl silicone resin or methyphenylsiloxane for instance.

[0014] The invention relates as well to a process for the preparation of the polymeric composition, comprising the following steps:

a) mixing (I) a resin containing the phenolic groups and the reticulation agent, (II) a resin containing the terminal silanol groups, and (III) an epoxy resin or the epoxidised organopolysiloxane

b) curing the mixture for a period of time sufficient to substantially complete the reaction between the phenolic groups and the terminal silanol groups,

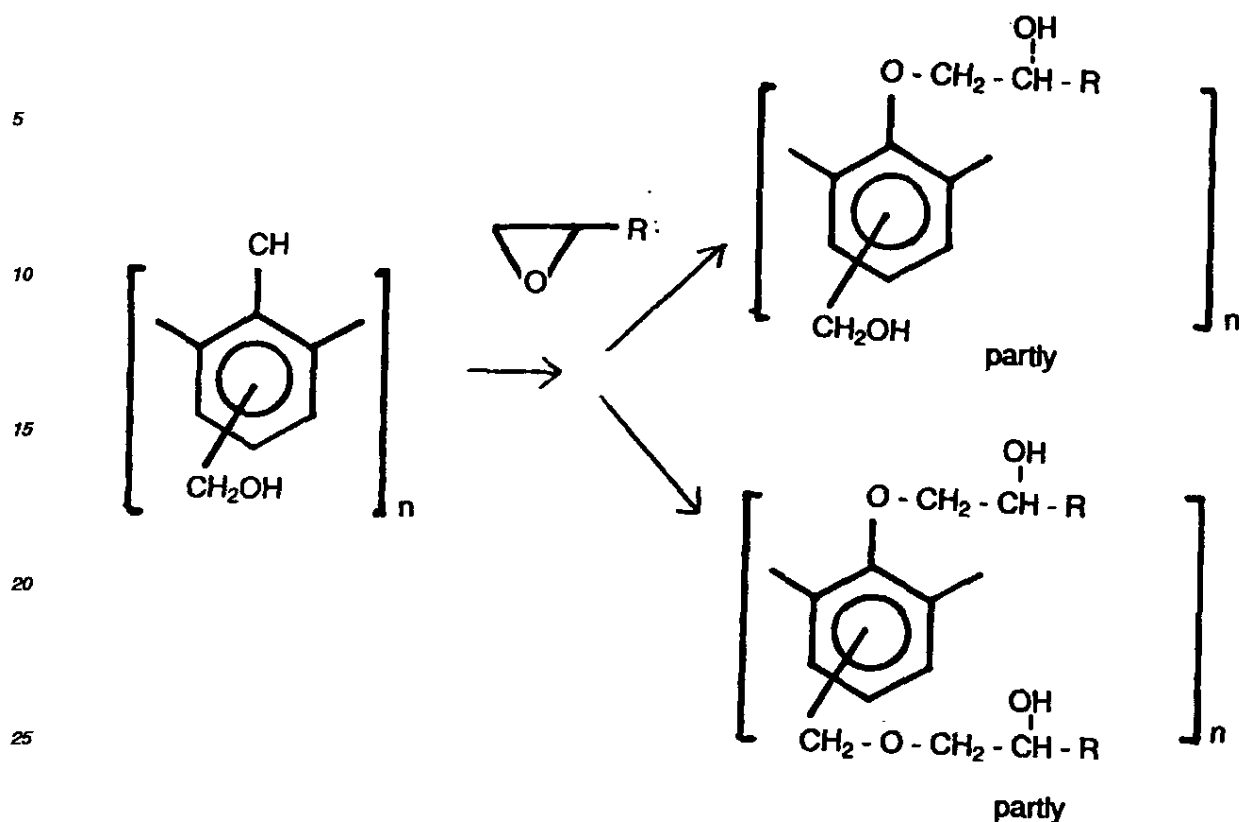
c) post-heating the product obtained under b).

[0015] It should be noted that the reaction is made in the presence of an epoxy resin or an epoxidised organopolysiloxane. This will push the reaction towards the way of a condensation or co-reaction leading to a copolymer rather than a simple homoreaction between the silicone resin and itself as mentioned above for the prior art.

[0016] Such a reaction involving the epoxy resin may be symbolised as follows:







[0017] The silicone resin is present in the starting mixture from 10 to 20 % by weight , preferably around 20%. The epoxy resin may be for instance of <sup>®</sup>Ciba-Geigy (GT 7071) type and may be present in the starting mixture from 20 to 40 % by weight. The epoxidised organopolysiloxane may be for instance a polydialkylsiloxane and may be present in the starting mixture from 3 to 10%, but preferably around 5%

[0018] To make easier the blending of the starting resins, said resins are preferably in a form of powder with a particle size distribution of not more than 400  $\mu\text{m}$ , preferably below 300  $\mu\text{m}$  for a compound such as <sup>®</sup>Xylok cited above, and 200  $\mu\text{m}$  for silicone.

[0019] The mixing step a) which may be held as well as a step for forming or shaping the end product is preferably conducted in a mould at a temperature not exceeding 50°C.

[0020] In general, the curing step b) is conducted under a pressure of at least 50 atm and a temperature from 80 to 160°C and may be divided in a number of cycles permitting the degassing of the reaction mixture. In this case each degassing cycle is most preferably performed in sequence at increasing pressures and temperatures.

[0021] As to the post-heating step c) the temperature is advantageously of at least 200°C, under atmospheric pressure.

[0022] The various objects and advantages of the invention will become apparent with regard to the following non limitative examples.

#### EXAMPLES 1 TO 7

[0023] From a starting blend containing 20% epoxy resin GT 7071, 10% silicone resin 6-2230 and 70%<sup>®</sup>Xylok, samples of 10 x 60 mm (table 1) were fabricated following the conditions described below.

Step 0: At least 60 s at the curing temperatures without pressure

Step 1: 5 degassing cycles with a pressure of 146 atm (6 s on, 10 s off) at the curing temperatures for 5, 12, 17.5, 23, or 30 minutes respectively at the curing temperature with a pressure of 183 atm.

Step 2: 10 minutes at 160°C with 3 degassing cycles (6 s on, 10 s off)



Table 1

Example	Curing temperature (°C)	Time (min)
1	80	23
2	80	12
3	150	23
4	150	12
5	115	5
6	115	30
7	115	17.5

[0024] Specimens of these formulations were submitted to different post-curing temperatures of 200°C and 240°C and processed with a brake pad with the usual additional ingredients, to form specific formulations for water tests.

[0025] The water absorption was tested using a method, where a 10 µl water drop is deposited at the surface of the sample and the time for absorption is recorded (table 2). On a <sup>®</sup>Teflon surface, which was used as a reference, a 10 µl drop was evaporated in 60 minutes.

Table 2

Examples	Curing Temperature (°C)	Post-curing at 200°C	Post-curing at 240°C
2	80	55 min	61 min
3	115	62 min	74 min
6	150	63 min	67 min

[0026] The results showed that the time needed for the water to disappear corresponds to almost that for its evaporation, which confirms that the water absorption for these resin formulations is very low.

[0027] After a heat treatment to 350°C, which was intended to simulate heating and over heating by breaking, the following comparative results were obtained for formulations post-cured at 240°C.

[0028] With specific formulations (resin and other conventional brake pad ingredients) prepared for water tests, the time needed for water to disappear (absorber or evaporated) for pure <sup>®</sup>Xylok correspond to 12 s and to 10 s after heating at 350°C for 1h and 2 h respectively. The corresponding times for the specific formulations according to the invention, were at 407 s after 1h heating at 350°C and 186 s after 2h heating at 350°C.

[0029] Several reactions could be expected between the different compounds of the formulations:

- the OH end groups of the Xylok could react with the epoxy groups of GT 7071 resin allowing the formation of a C-O-CH<sub>2</sub>-CHOH- bond,
- the OH end groups of the Xylok could react with those of the polydimethyl siloxane 6-2230 leading to the formation of a Si-C-O bond.

[0030] Infra-red evidence of the formation of those groups should be the reduction of the phenyl-CH<sub>2</sub>-OH characteristic band near 1010 cm<sup>-1</sup> as well as the appearance of the typical bands of Si-C-O bond near 1100 cm<sup>-1</sup> (asymmetric stretching vibrations) and C-O-CH<sub>2</sub> bond near 1040 cm<sup>-1</sup>.

[0031] The time and temperature of exposure before curing (step 1) are important to the extent of reaction between silicone-hydroxyl and <sup>®</sup>Xylok-hydroxyl groups. Hence, the change in the peaks were studied as a function of pre-curing temperature and time. Table 3 (reference bands with regards to starting resins) and Table 4 below summarise the characteristic bands for each IR spectrum.



Table 3

Bands/Samples	Epoxy groups, 835 cm <sup>-1</sup>	Si-O-C 850 cm <sup>-1</sup>	Si-OH 900 cm <sup>-1</sup>	$\phi$ CH <sub>2</sub> OH 1010 cm <sup>-1</sup>	Si-O-C or C-O-C 1100 cm <sup>-1</sup>	-C=O 1650 cm <sup>-1</sup>	-CH- 3000 cm <sup>-1</sup>	-OH 3100-3600 cm <sup>-1</sup>
<sup>®</sup> Xylok	none	none	none	strong	weak	none	strong	strong
Silicone resin	none	none	strong	none	strong	none	weak	weak
Epoxy resin	strong	none	none	none	weak	none	strong	weak

[0032] Table 4 relates to formulations where step 0 was conducted at 80°C, with comparison to samples where step 0 was conducted of 12 min at 80°C respectively with no curing or post-curing (3rd column in table).

Table 4

Conditions			Epoxy groups	Si-O-C	Si-OH	$\phi$ CH <sub>2</sub> OH	Si-O-C or C-O-C	-C=O	-CH-	-OH
Reaction time	Curing	Post-curing	835 cm <sup>-1</sup>	850 cm <sup>-1</sup>	900 cm <sup>-1</sup>	1010 cm <sup>-1</sup>	1100 cm <sup>-1</sup>	1650 cm <sup>-1</sup>	3000 cm <sup>-1</sup>	3100-3600 cm <sup>-1</sup>
12 min	no	no	strong	none	weak	strong	strong	none	strong	strong
12 min	no	no	stronger	none	weak	smaller	strong	none	stronger	stronger
12 min	165°C	no	stronger	none	smaller	smaller	stronger	none	strong	lower
12 min	165°C	240°C	stronger	none	smaller	smaller	stronger	strong	strong	strong
23 min	165°C	240°C	stronger	none	smaller	smaller	stronger	stronger	strong	strong

#### EXAMPLES 8 TO 14

[0033] From a starting blend containing 5% of epoxidised solution of Dow Corning sold under the name of Additive 23, 20% silicone resin 6-2230 and 75% <sup>®</sup>Xylok, 10 x 60 mm samples (table 1) were fabricated following the conditions described below.

Step 0: At least 1.5 min at the curing temperatures without pressure

Step 1: 5 degassing cycles with a pressure of 148 atm (6 s on, 10 s off) at the curing temperatures. 12, 17.5 or 30 minutes at the curing temperature with a pressure of 183 atm.

Step 2: 10 minutes at 160°C with 3 degassing cycles (6 s on, 10 s off)

Table 5

Examples	Curing temperature (°C)	Time (min)
8	140	23
9	140	12
10	160	23
11	160	12
12	150	5
13	150	30



Table 5 (continued)

Examples	Curing temperature (°C)	Time (min)
14	150	17.5

[0034] Specimens of these formulations were submitted to different post-curing temperatures of 200°C and 240°C and processed with a brake pad with the usual additional ingredients, to form specific formulations for water tests.

[0035] The water absorption was again tested as for the formulations of the previous examples 1 to 7 using the above method of water droplet. As a result, the formulations as presented below, showed similar behaviour to that of the previous examples.

Table 6

Examples	Curing Temperature (°C)	Reaction time (min)	Post-curing at 200°C	Post-curing at 240°C
9	140	12	70 min	72 min
10	150	17.5	80 min	77 min
14	160	23	77 min	66 min

[0036] The results showed that the time needed for the water to disappear corresponds to almost that for its evaporation, which confirms that the water absorption for these resin formulations is very low.

[0037] After a heat treatment to 350°C, which was intended to simulate heating and over heating by breaking, the following comparative results were obtained for formulations post-cured at 240°C.

[0038] With specific formulations (resin and other conventional brake pad ingredients) prepared for water tests, the time needed for water to disappear (absorbed or evaporated) for pure ©Xylox correspond to 12 s and to 10 s after heating at 350°C for 1 h and 2 h respectively. The corresponding times for the specific formulations according to the invention, were 1'972 s after 1 h heating at 350°C and 1'832 s after 2 h heating at 350°C.

[0039] Also, if time needed for the water to disappear (absorbed or evaporated) correspond to 100% for the respective above inventive formulations as crude samples (no treatment to 350°C), then after 1 h of heating to 350°C these specific formulations for water tests were at 75 %, 98 % and 98 % respectively for pure ©Xylox, Mitsui product (©Xylox plus Si) and the inventive formulations.

[0040] However, after 2 h of heating at 350°C, the results were 63 %, 53 % and 87 % respectively for pure ©Xylox, Mitsui product (©Xylox plus Si) and the inventive formulations.

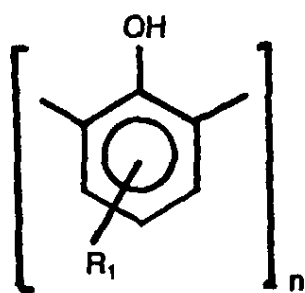
[0041] These results indicate the excellent performance and good resistance of the inventive resin formulations to prolonged heat treatments as compared to pure ©Xylox or even the Mitsui product (©Xylox plus Si).

#### Claims

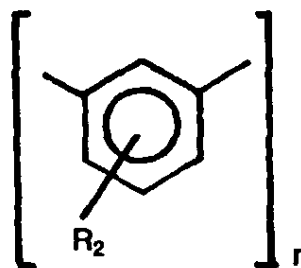
1. A polymeric composition for friction elements, comprising a co-polymer between (I) a resin containing phenolic groups and a reticulation agent, and (II) an organopolysiloxane resin containing terminal silanol groups, a part at least of the phenolic groups being bound to the terminal silanol groups.
2. A polymeric composition according to claim 1, wherein the resin comprising phenolic group comprises also terminal non aromatic alcoholic groups, a part at least of the terminal non aromatic alcoholic groups being bound to the terminal silanol groups.
3. A polymeric composition according to claim 1 or 2, which comprises an epoxy resin or an epoxidised organopolysiloxane (III).
4. A polymeric composition according to any of the preceding claims, in which the resin (I) containing phenolic groups is of general formula (A) and may include moieties of the general formula (A'):







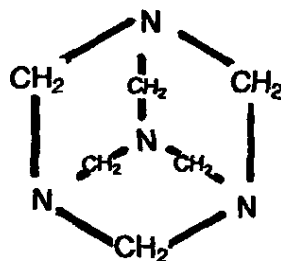
A



A'

$R_1$  or  $R_2 = \text{H, Alkyl, } -\text{CH}_2\text{OH}$

5. A polymeric composition according to any of the preceding claims, in which the organopolysiloxane resin (II) containing terminal silanol groups is a hydroxy phenyl alkyl silicone resin.
6. A polymeric composition according to any of the preceding claims, in which the reticulation agent is an hexamine of general formula (B):



7. A process of preparation of a polymeric composition according to any of the preceding claims, comprising the following steps:
- a) mixing (I) a resin containing the phenolic groups and the reticulation agent, (II) resin containing the terminal silanol groups, and (III) an epoxy resin or the epoxidised organopolysiloxane
  - b) curing the mixture for a period of time sufficient to complete substantially the reaction between the phenolic groups and the terminal silanol groups,
  - c) post-heating the product obtained under b).
8. A process according to claim 7. in which the mixing step a) is conducted at a temperature not exceeding 50°C.
9. A process according to claim 8, in which the curing step b) is conducted under a pressure of at least 50 atm and the temperature is from 80 to 160°C.
10. A process according to claim 7. in which the curing step b) is divided in a number of cycles permitting the degassing of the reaction mixture.
11. A process according to claim 10, in which each degassing cycle is conducted in sequence at increasing pressure



and temperature.

**12.** A process according to claim 7 in which the post-heating step c) is conducted at a temperature of at least 200°C under atmospheric pressure.

5

**13.** A process according to claim 7 in which the starting resins are in a form of powder with a particle size distribution of not more than 400 µm

**14.** The use of the polymeric composition of any of claims 1 to 6 as a substrate for brake pads

10

15

20

25

30

35

40

45

50

55





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number  
EP 98 42 0024

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US 4 657 951 A (TAKARADA MITSUHIRO ET AL) 14 April 1987 * claims 1-6 *	1,2,4-6, 14	C08G77/42 C08L83/10 C08L61/06
X	US 3 911 045 A (HARTMANN PETER ET AL) 7 October 1975 * claim 1 * * column 2, line 33 - line 60 *	1	
X	WO 96 33238 A (AMERON INC ;KANE JOHN F (US); MOHRER NORMAN R (US)) 24 October 1996 * claims 1-43 * * page 3, line 3 - line 4 * * page 16, line 16 - line 31 * * page 36, line 25 - line 30 *	1,2,4-6	
A	WO 97 19977 A (BP CHEM INT LTD) 5 June 1997 * claims 1-10 *	1	
X	DE 16 94 974 A (STENBECK G) 26 August 1971 * claim 1 * * page 1, paragraph 3 * * page 3; example 1 *	1	
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>28 May 1998</b>	Examiner <b>Depijper, R</b>
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			



**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 42 0024

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

28-05-1998

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4657951 A	14-04-1987	JP 2015978 C	19-02-1996
		JP 6092524 B	16-11-1994
		JP 61192711 A	27-08-1986
US 3911045 A	07-10-1975	DE 2306463 A	29-08-1974
		AU 476576 B	30-09-1976
		AU 6525674 A	07-08-1975
		BE 810720 A	07-08-1974
		CA 1033491 A	20-06-1978
		CS 175473 B	31-05-1977
		DD 111395 A	12-02-1975
		FR 2217376 A	06-09-1974
		GB 1424290 A	11-02-1976
		JP 1047903 C	28-05-1981
		JP 49113000 A	28-10-1974
		JP 55039183 B	08-10-1980
		NL 7401649 A	13-08-1974
		ZA 7400835 A	24-12-1974
WO 9633238 A	24-10-1996	US 5736619 A	07-04-1998
		AU 5558396 A	07-11-1996
		EP 0821711 A	04-02-1998
		NO 974832 A	22-12-1997
		PL 322898 A	02-03-1998
WO 9719977 A	05-06-1997	AU 7582896 A	19-06-1997
DE 1694974 A	26-08-1971	NONE	





## PATENT COOPERATION TREATY

PCT

NOTIFICATION OF THE INTERNATIONAL  
APPLICATION NUMBER AND OF THE  
INTERNATIONAL FILING DATE

(PCT Rule 20.5(c))

From the RECEIVING OFFICE

To:

MOINAS, Michel  
Moinas, Savoye & Cronin  
42, rue Plantamour  
CH-1201 Geneva  
SUISSE

Date of mailing (day/month/year) 08 February 1999 (08.02.99)		IMPORTANT NOTIFICATION	
Applicant's or agent's file reference M150/WO/005			
International application No. PCT/IB99/00207	International filing date (day/month/year) 08 February 1999 (08.02.99)	Priority date (day/month/year) 09 February 1998 (09.02.98)	
Applicant M3D SOCIETE ANONYME et al			
Title of the invention A POLYMERIC COMPOSITION FOR FRICTION ELEMENTS			

1. The applicant is hereby notified that the international application has been accorded the international application number and the international filing date indicated above.

2. The applicant is further notified that the record copy of the international application:

- ☒ was transmitted to the International Bureau on 08 February 1999 (08.02.99)
- ☐ has not yet been transmitted to the International Bureau for the reason indicated below and a copy of this notification has been sent to the International Bureau\*:
- ☐ because the necessary national security clearance has not yet been obtained.
- ☐ because (reason to be specified):

The International Bureau monitors the transmittal of the record copy by the receiving Office and will notify the applicant with Form PCT/IB/301) of its receipt. Should the record copy not have been received by the expiration of 14 months from the priority date, the International Bureau will notify the applicant (Rule 22.1(c)).

Mailing address of the receiving Office  
International Bureau of WIPO  
PCT Receiving Office Section  
Les Colombettes, 1211 Geneva 20, Switzerland  
(41-22) 910 06 10 (Groups 3 and 4)

Authorised officer

*Ann*  
Agnes Wittmann-Regis

Telephone No (41-22) 338 90 33





## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C08G 77/42, C08L 83/10, 61/06</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/40146</b>  <b>(43) International Publication Date:</b> 12 August 1999 (12.08.99)
<b>(21) International Application Number:</b> PCT/IB99/00207 <b>(22) International Filing Date:</b> 8 February 1999 (08.02.99)  <b>(30) Priority Data:</b> 98420024.6                      9 February 1998 (09.02.98)                      EP  <b>(71) Applicant (for all designated States except US):</b> M3D SOCI- ETE ANONYME [FR/FR]; 16B, rue des Jardins, F-74240 Gaillard (FR).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> KANELLOPOULOS, Vasilios [CH/CH]; 6, chemin Sous-le-Crêt, CH-1256 Troinex (CH). LOUIS-JOSEPH-DOGUE, Isabelle [FR/FR]; 43, rue du Dr Coquand, F-74100 Annemasse (FR). McGINNISS, Vincent, Daniel [US/US]; P.O. Box 702, Sunbury, OH 43074 (US). MANGARAJ, Duryodhan [US/US]; 7828, Backjack Court, Dublin, OH 43017 (US). NAKAMURA, Tomoki [JP/JP]; Tsuchiya, Narita, Chiba 892-11 (JP).  <b>(74) Agents:</b> MOINAS, Michel et al.; Moinas Savoye & Cronin, 42, rue Plantamour, CH-1201 Geneva (CH).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> A POLYMERIC COMPOSITION FOR FRICTION ELEMENTS  <b>(57) Abstract</b>  The polymeric composition for friction elements comprises a co-polymer between (I) a resin containing phenolic groups and a reticulation agent, and (II) an organopolysiloxane resin containing terminal silanol groups. A part at least of the phenolic groups is bound to the terminal silanol groups. A process of the preparation of the above polymeric composition may comprise the following steps: a) mixing (I) a resin containing the phenolic groups and the reticulation agent, (II) resin containing the terminal silanol groups, and (III) an epoxy resin or the epoxidised organopolysiloxane; b) curing the mixture for a period of time sufficient to complete substantially the reaction between the phenolic groups and the terminal silanol groups, c) post-heating the product obtained under b).		

•

.

.

.

.

.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		



# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/IB 99/00207

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08G77/42 C08L83/10 C08L61/06

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 657 951 A (TAKARADA MITSUHIRO ET AL) 14 April 1987 see claims 1-6 ---	1,2,4-6, 14
X	US 3 911 045 A (HARTMANN PETER ET AL) 7 October 1975 see claim 1 see column 2, line 33 - line 60 ---	1
X	WO 96 33238 A (AMERON INC ;KANE JOHN F (US); MOWRER NORMAN R (US)) 24 October 1996 see claims 1-43 see page 3, line 3 - line 4 see page 16, line 16 - line 31 see page 36, line 25 - line 30 --- -/--	1,2,4-6

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

21 April 1999

Date of mailing of the international search report

04/05/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Depijper, R





# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/IB 99/00207

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 19977 A (BP CHEM INT LTD) 5 June 1997 see claims 1-10 ---	1
X	DE 16 94 974 A (STENBECK G) 26 August 1971 see claim 1 see page 1, paragraph 3 see page 3; example 1 -----	1



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 99/00207

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4657951	A	14-04-1987	JP 2015978 C	19-02-1996
			JP 6092524 B	16-11-1994
			JP 61192711 A	27-08-1986
US 3911045	A	07-10-1975	DE 2306463 A	29-08-1974
			AU 476576 B	30-09-1976
			AU 6525674 A	07-08-1975
			BE 810720 A	07-08-1974
			CA 1033491 A	20-06-1978
			CS 175473 B	31-05-1977
			DD 111395 A	12-02-1975
			FR 2217376 A	06-09-1974
			GB 1424290 A	11-02-1976
			JP 1047903 C	28-05-1981
			JP 49113000 A	28-10-1974
			JP 55039183 B	08-10-1980
			NL 7401649 A	13-08-1974
			ZA 7400835 A	24-12-1974
WO 9633238	A	24-10-1996	US 5736619 A	07-04-1998
			AU 699446 B	03-12-1998
			AU 5558396 A	07-11-1996
			BR 9608196 A	21-07-1998
			CA 2218694 A	24-10-1996
			CZ 9703331 A	17-06-1998
			EP 0821711 A	04-02-1998
			HU 9802381 A	01-02-1999
			JP 10506956 T	07-07-1998
			NO 974832 A	22-12-1997
			NZ 306894 A	28-07-1998
			PL 322898 A	02-03-1998
WO 9719977	A	05-06-1997	AU 7582896 A	19-06-1997
			EP 0861282 A	02-09-1998
			NO 982433 A	28-07-1998
			US 5864000 A	26-01-1999
DE 1694974	A	26-08-1971	NONE	

• • • •

!

4

•

•

•

•

•

!

•

•

•

# PATENT COOPERATION TREATY

7 JUL. 2000

**PCT**

From the INTERNATIONAL BUREAU

## NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

To:

MOINAS, Michel  
Moinas Savoye & Cronin  
42, rue Plantamour  
CH-1201 Geneva  
SUISSE

Date of mailing (day/month/year)

03 July 2000 (03.07.00)

Applicant's or agent's file reference

M150/WO/005

### IMPORTANT NOTIFICATION

International application No.

PCT/IB99/00207

International filing date (day/month/year)

08 February 1999 (08.02.99)

1. The following indications appeared on record concerning:



the applicant



the inventor



the agent



the common representative

Name and Address

M3D SOCIETE ANONYME  
16B, rue des Jardins  
F-74240 Gaillard  
France

State of Nationality

FR

State of Residence

FR

Telephone No.

+33 4 5043 2000

Facsimile No.

+33 4 5043 2001

Teleprinter No.

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:



the person



the name



the address



the nationality



the residence

Name and Address

NISSHINBO INDUSTRIES, INC.  
31-11, Nihonbashi Ningyocho 2-chome  
Chuo-ku  
Tokyo 103-8650  
Japan

State of Nationality

JP

State of Residence

JP

Telephone No.

Facsimile No.

Teleprinter No.

3. Further observations, if necessary:

Please be informed that a power of attorney is still missing. *OK*

4. A copy of this notification has been sent to:



the receiving Office



the International Searching Authority



the International Preliminary Examining Authority



the designated Offices concerned



the elected Offices concerned



other:

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Authorized officer

*C. Carrié*  
Christine Carrié

Facsimile No.: (41-22) 740.14.35

Telephone No.: (41-22) 338.83.38



# PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>M150/WO/005</b>	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/PEA/416)	
International application No. <b>PCT/IB99/00207</b>	International filing date (day/month/year) <b>08/02/1999</b>	Priority date (day/month/year) <b>09/02/1998</b>
International Patent Classification (IPC) or national classification and IPC <b>C08G77/42</b>		
Applicant <b>M3D SOCIETE ANONYME et al</b>		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.


2. This REPORT consists of a total of 5 sheets, including this cover sheet.

☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand  <b>03/09/1999</b>	Date of completion of this report  <b>16.05.2000</b>
Name and mailing address of the international preliminary examining authority:   <b>European Patent Office</b> <b>D-80298 Munich</b> <b>Tel. +49 89 2399 - 0 Tx: 523656 epmu d</b> <b>Fax: +49 89 2399 - 4465</b>	Authorized officer  <b>Idez, C</b>  Telephone No. <b>+49 89 2399 8665</b>







# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IB99/00207

## I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

### Description, pages:

1-9 as originally filed

### Claims, No.:

1-14 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. Statement

Novelty (N)	Yes:	Claims	1-14
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-14
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-14
	No:	Claims	



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/IB99/00207

---

2. Citations and explanations

**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**



1) Concerning point V:

1.1) Reference is made to the following document:

D1 = US-A-4657951

1.2) D1 discloses compositions comprising a phenolic resin modified by reaction with an hydroxyl group containing polysiloxane resin and a reticulation agent for the phenolic resin ( for example hexamethylene tetramine). These compositions are cured at a temperature between 150 to 200°C under a pressure in the range of 150 to 300 kg/cm<sup>2</sup> and are used in the manufacture of friction elements. ( see D1, claims 1, 3, 4, 5, column 3, line 7 to column 4, line 61).

Since D1 does not disclose the use of an epoxy resin or of an epoxidised organopolysiloxane in the compositions, the subject-matter of present claims 1 to 14 is considered as novel over D1. (Art.33(2)).

1.3) The main difference between the compositions disclosed in the present application and D1 is the fact that they contain an epoxy resin or an epoxidised organopolysiloxane.

1.4) The Applicant has shown, that the addition of an epoxy resin leads to compositions having a lower water absorption and better friction resistance under wet conditions. These effects cannot have been foreseen from the documents cited in the search report. Thus, inventive step can be acknowledged for the subject-matter of present claims 1 to 14. (Art.33(3)).

2) Concerning point VIII:

2.1) Lines 5 to 9 on page 2 of the description are not in accordance with present claim 1. ( Art.6).



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/IB99/00207

2.2) The wording "reticulation agent " used in present claims 1 and 7 is vague, since it is not indicated which resin this "reticulation agent" should crosslink ( epoxy resin, phenolic resin..). (Art.6).

2.3) The wording "an hexamine" used in present claim 6 is unclear, since hexamine is the hexamethylene tetramine. (Art.6).

2.4) It is unclear how the reaction of a **silanol** group with a **phenolic** group can lead to a bond Si-C-O ( see page 6, lines 28-29). (Art.6).





## PCT REQUEST

1/5

M150/WO/005

Original (for SUBMISSION) - printed on 05.02.1999 04:13:21 PM

0	For receiving Office use only	
0-1	International Application No.	
0-2	International Filing Date	
0-3	Name of receiving Office and "PCT International Application"	
0-4	Form - PCT/RO/101 PCT Request Prepared using	PCT-EASY Version 2.82 (updated 01.01.1999)
0-5	Petition The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty	
0-6	Receiving Office (specified by the applicant)	International Bureau of the World Intellectual Property Organization (RO/IB)
0-7	Applicant's or agent's file reference	M150/WO/005
I	Title of invention	A POLYMERIC COMPOSITION FOR FRICTION ELEMENTS
II	Applicant	
II-1	This person is:	applicant only
II-2	Applicant for	all designated States except US
II-4	Name	M3D SOCIETE ANONYME
II-5	Address:	16B, rue des Jardins F-74240 Gaillard France
II-6	State of nationality	FR
II-7	State of residence	FR
II-8	Telephone No.	+33 4 5043 2000
II-9	Facsimile No.	+33 4 5043 2001
II-10	e-mail	m3d@wanadoo.fr
III-1	Applicant and/or inventor	
III-1-1	This person is:	applicant and inventor
III-1-2	Applicant for	US only
III-1-4	Name (LAST, First)	KANELLOPOULOS, Vasilios
III-1-5	Address:	6, chemin Sous-le-Crêt CH-1256 Troinex Switzerland
III-1-6	State of nationality	CH
III-1-7	State of residence	CH



## PCT REQUEST

Original (for SUBMISSION) - printed on 05.02.1999 04:13:21 PM

III-2	Applicant and/or inventor	
III-2-1	This person is:	applicant and inventor
III-2-2	Applicant for	US only
III-2-4	Name (LAST, First)	LOUIS-JOSEPH-DOGUE, Isabelle
III-2-5	Address:	43, rue du Dr Coquand F-74100 Annemasse France
III-2-6	State of nationality	FR
III-2-7	State of residence	FR
III-3	Applicant and/or inventor	
III-3-1	This person is:	applicant and inventor
III-3-2	Applicant for	US only
III-3-4	Name (LAST, First)	MCGINNIS, Vincent Daniel
III-3-5	Address:	P.O. Box 702 Sunbury, OH 43074 United States of America
III-3-6	State of nationality	US
III-3-7	State of residence	US
III-4	Applicant and/or inventor	
III-4-1	This person is:	applicant and inventor
III-4-2	Applicant for	US only
III-4-4	Name (LAST, First)	MANGARAJ, Duryodhan
III-4-5	Address:	7828, Backjack Court Dublin, OH 43017 United States of America
III-4-6	State of nationality	US
III-4-7	State of residence	US
III-5	Applicant and/or inventor	
III-5-1	This person is:	applicant and inventor
III-5-2	Applicant for	US only
III-5-4	Name (LAST, First)	NAKAMURA, Tomoki
III-5-5	Address:	Tsuchiya Narita, Chiba 892-11 Japan
III-5-6	State of nationality	JP
III-5-7	State of residence	JP



## PCT REQUEST

3/5

M150/WO/005

Original (for SUBMISSION) - printed on 05.02.1999 04:13:21 PM

IV-1	Agent or common representative; or address for correspondence The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:	agent
IV-1-1	Name (LAST, First)	MOINAS, Michel
IV-1-2	Address:	Moinas Savoye & Cronin 42, rue Plantamour CH-1201 Geneva Switzerland
IV-1-3	Telephone No.	+41 22 731 93 50
IV-1-4	Facsimile No.	+41 22 738 70 56
IV-1-5	e-mail	info@msc-ip.com
IV-2	Additional agent(s)	additional agent(s) with same address as first named agent
IV-2-1	Name(s)	SAVOYE, Jean-Paul; CRONIN, Brian
V	Designation of States	
V-1	Regional Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AP: GH GM KE LS MW SD SZ UG ZW and any other State which is a Contracting State of the Harare Protocol and of the PCT EA: AM AZ BY KG KZ MD RU TJ TM and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT EP: AT BE CH&LI CY DE DK ES FI FR GB GR IE IT LU MC NL PT SE and any other State which is a Contracting State of the European Patent Convention and of the PCT OA: BF BJ CF CG CI CM GA GN GW ML MR NE SN TD TG and any other State which is a member State of OAPI and a Contracting State of the PCT
V-2	National Patent (other kinds of protection or treatment, if any, are specified between parentheses after the designation(s) concerned)	AL AM AT AU AZ BA BB BG BR BY CA CH&LI CN CU CZ DE DK EE ES FI GB GD GE GH GM HR HU ID IL IN IS JP KE KG KP KR KZ LC LK LR LS LT LU LV MD MG MK MN MW MX NO NZ PL PT RO RU SD SE SG SI SK SL TJ TM TR TT UA UG US UZ VN YU ZW



## PCT REQUEST

Original (for SUBMISSION) - printed on 05.02.1999 04:13:21 PM

V-5	Precautionary Designation Statement In addition to the designations made under items V-1, V-2 and V-3, the applicant also makes under Rule 4.9(b) all designations which would be permitted under the PCT except any designation(s) of the State(s) indicated under item V-6 below. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit.	
V-6	Exclusion(s) from precautionary designations	NONE
VI-1	Priority claim of earlier regional application	
VI-1-1	Filing date	09 February 1998 (09.02.1998)
VI-1-2	Number	98420024.6
VI-1-3	Regional Office	EP
VII-1	International Searching Authority Chosen	European Patent Office (EPO) (ISA/EP)
VII-2	Request to use results of earlier search; reference to that search	
VII-2-1	Date	10 June 1998 (10.06.1998)
VII-2-2	Number	98420024.6-2115
VII-2-3	Country (or regional Office)	EP
VIII	Check list	number of sheets      electronic file(s) attached
VIII-1	Request	5      -
VIII-2	Description	9      -
VIII-3	Claims	3      -
VIII-4	Abstract	1      m150 005.txt
VIII-5	Drawings	0      -
VIII-7	TOTAL	18
VIII-8	Accompanying items	paper document(s) attached      electronic file(s) attached
VIII-8	Fee calculation sheet	✓      -
VIII-10	PCT-EASY diskette	-      diskette
VIII-18	Figure of the drawings which should accompany the abstract	
VIII-18	Language of filing of the international application	English
IX	Signature of applicant or agent	
IX-1	Name (LAST, First)	
IX-2	Capacity	

FOR RECEIVING OFFICE USE ONLY

10-1	Date of actual receipt of the purported international application	
------	---	--





# PATENT COOPERATION TREATY

From the:  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

REQU le  
28 NOV. 1999

**PCT** Rep:.....

To:

MOINAS Michel  
MOINAS SAVOYE & CRONIN  
Rue Plantamour 42  
CH-1201 Geneva  
SUISSE

**WRITTEN OPINION**

(PCT Rule 66)

Date of mailing  
(day/month/year) **26. 11. 99**

Applicant's or agent's file reference

**M150/WO/005**

**REPLY DUE**

**within 3 month(s)**  
from the above date of mailing

International application No.

**PCT/IB99/00207**

International filing date (day/month/year)

**08/02/1999**

Priority date (day/month/year)

**09/02/1998**

International Patent Classification (IPC) or both national classification and IPC

**C08G77/42**

Applicant

**M3D SOCIETE ANONYME et al**

1. This written opinion is the first drawn up by this International Preliminary Examining Authority.

2. This opinion contains indications relating to the following items:

- I ☒ Basis of the opinion
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain document cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

3. The applicant is hereby invited to reply to this opinion.

**When?** See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

**How?** By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

**Also:** For an additional opportunity to submit amendments, see Rule 66.4.  
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis.  
For an informal communication with the examiner, see Rule 66.6.

**If no reply is filed,** the international preliminary examination report will be established on the basis of this opinion.

4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: **09/06/2000.**

Name and mailing address of the international preliminary examining authority:



European Patent Office  
D-80298 Munich  
Tel. +49 89 2399 - 0 Tx: 523656 epmu d  
Fax +49 89 2399 - 4465

Authorized officer / Examiner

**Idez, C**

Formalities officer (incl. extension of time limits)

**Aperribay, I**

Telephone No. 49 89 2399 8154





**1. Basis of the opinion**

1. This opinion has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed".*):

**Description, pages:**

1-9 as originally filed

**Claims, No.:**

1-14 as originally filed

**2. The amendments have resulted in the cancellation of:**

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

3. This opinion has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

**4. Additional observations, if necessary:**

**V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Claims	
Inventive step (IS)	Claims	1-14 no
Industrial applicability (IA)	Claims	

**2. Citations and explanations**

**see separate sheet**



**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**



**1) Concerning point V:**

**1.1) Reference is made to the following document:**

**D1 = US-A-4657951**

**1.2) D1 discloses compositions comprising a phenolic resin modified by reaction with an hydroxyl group containing polysiloxane resin and a reticulation agent for the phenolic resin ( for example hexamethylene tetramine). These compositions are cured at a temperature between 150 to 200°C under a pressure in the range of 150 to 300 kg/cm<sup>2</sup> and are used in the manufacture of friction elements. ( see D1, claims 1, 3, 4, 5, column 3, line 7 to column 4, line 61).**

**Since D1 does not disclose the use of an epoxy resin or of an epoxidised organopolysiloxane in the compositions, the subject-matter of present claims 1 to 14 is considered as novel over D1. (Art.33(2)).**

**1.3) The main difference between the compositions disclosed in the present application and D1 is the fact that they contain an epoxy resin or an epoxidised organopolysiloxane.**

**1.4) It is presently unclear which technical problem is solved in an unexpected manner by adding this epoxy component to the compositions of D1. Inventive step cannot presently be acknowledged for the subject-matter of present claims 1 to 14.**

**2) Concerning point VIII:**

**2.1) Lines 5 to 9 on page 2 of the description do not appear to be in accordance with present claim 1. ( Art.6).**

**2.2) The wording "reticulation agent " used in present claims 1 and 7 is vague,**





since it is not indicated which resin this "reticulation agent" should crosslink ( epoxy resin, phenolic resin..). (Art.6).

2.3) The wording "an hexamine" used in present claim 6 is unclear, since hexamine is the hexamethylene tetramine. (Art.6).

2.4) It is unclear how the reaction of a **silanol** group with a **phenolic** group can lead to a bond Si-C-O ( see page 6, lines 28-29). (Art.6).



17 MAI 2000

From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT

(PCT Rule 71.1)

To:

MOINAS Michel  
MOINAS SAVOYE & CRONIN  
Rue Plantamour 42  
CH-1201 Geneva  
SUISSE

Date of mailing  
(day/month/year) 16.05.2000

Applicant's or agent's file reference  
M150/WO/005

## IMPORTANT NOTIFICATION

International application No.  
PCT/IB99/00207

International filing date (day/month/year)  
08/02/1999

Priority date (day/month/year)  
09/02/1998

Applicant  
M3D SOCIETE ANONYME et al

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

## 4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/



European Patent Office  
D-80298 Munich  
Tel. +49 89 2399 - 0 Tx: 523656 epmu d  
Fax: +49 89 2399 - 4465

Authorized officer

Aperribay, I

Tel. +49 89 2399-8154





## PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference <b>M150/WO/005</b>	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. <b>PCT/IB99/00207</b>	International filing date (day/month/year) <b>08/02/1999</b>	Priority date (day/month/year) <b>09/02/1998</b>
International Patent Classification (IPC) or national classification and IPC <b>C08G77/42</b>		
Applicant <b>M3D SOCIETE ANONYME et al</b>		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 5 sheets, including this cover sheet.

- ☐ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand <b>03/09/1999</b>	Date of completion of this report <b>16.05.2000</b>
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer <b>Idez, C</b>  Telephone No +49 89 2399 8665 



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/IB99/00207

## I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

### Description, pages:

1-9 as originally filed

### Claims, No.:

1-14 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☐ the claims, Nos.:  
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

## V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

### 1. Statement

Novelty (N)	Yes:	Claims 1-14
	No:	Claims
Inventive step (IS)	Yes:	Claims 1-14
	No:	Claims
Industrial applicability (IA)	Yes:	Claims 1-14
	No:	Claims





**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/IB99/00207

---

**2. Citations and explanations**

**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/IB99/00207

**1) Concerning point V:**

**1.1) Reference is made to the following document:**

**D1 = US-A-4657951**

**1.2) D1 discloses compositions comprising a phenolic resin modified by reaction with an hydroxyl group containing polysiloxane resin and a reticulation agent for the phenolic resin ( for example hexamethylene tetramine). These compositions are cured at a temperature between 150 to 200°C under a pressure in the range of 150 to 300 kg/cm<sup>2</sup> and are used in the manufacture of friction elements. ( see D1, claims 1, 3, 4, 5, column 3, line 7 to column 4, line 61).**

**Since D1 does not disclose the use of an epoxy resin or of an epoxidised organopolysiloxane in the compositions, the subject-matter of present claims 1 to 14 is considered as novel over D1. (Art.33(2)).**

**1.3) The main difference between the compositions disclosed in the present application and D1 is the fact that they contain an epoxy resin or an epoxidised organopolysiloxane.**

**1.4) The Applicant has shown, that the addition of an epoxy resin leads to compositions having a lower water absorption and better friction resistance under wet conditions. These effects cannot have been foreseen from the documents cited in the search report. Thus, inventive step can be acknowledged for the subject-matter of present claims 1 to 14. (Art.33(3)).**

**2) Concerning point VIII:**

**2.1) Lines 5 to 9 on page 2 of the description are not in accordance with present claim 1. ( Art.6).**



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

---

International application No. PCT/IB99/00207

2.2) The wording "reticulation agent " used in present claims 1 and 7 is vague, since it is not indicated which resin this "reticulation agent" should crosslink ( epoxy resin, phenolic resin..). (Art.6).

2.3) The wording "an hexamine" used in present claim 6 is unclear, since hexamine is the hexamethylene tetramine. (Art.6).

2.4) It is unclear how the reaction of a **silanol** group with a **phenolic** group can lead to a bond Si-C-O ( see page 6, lines 28-29). (Art.6).

